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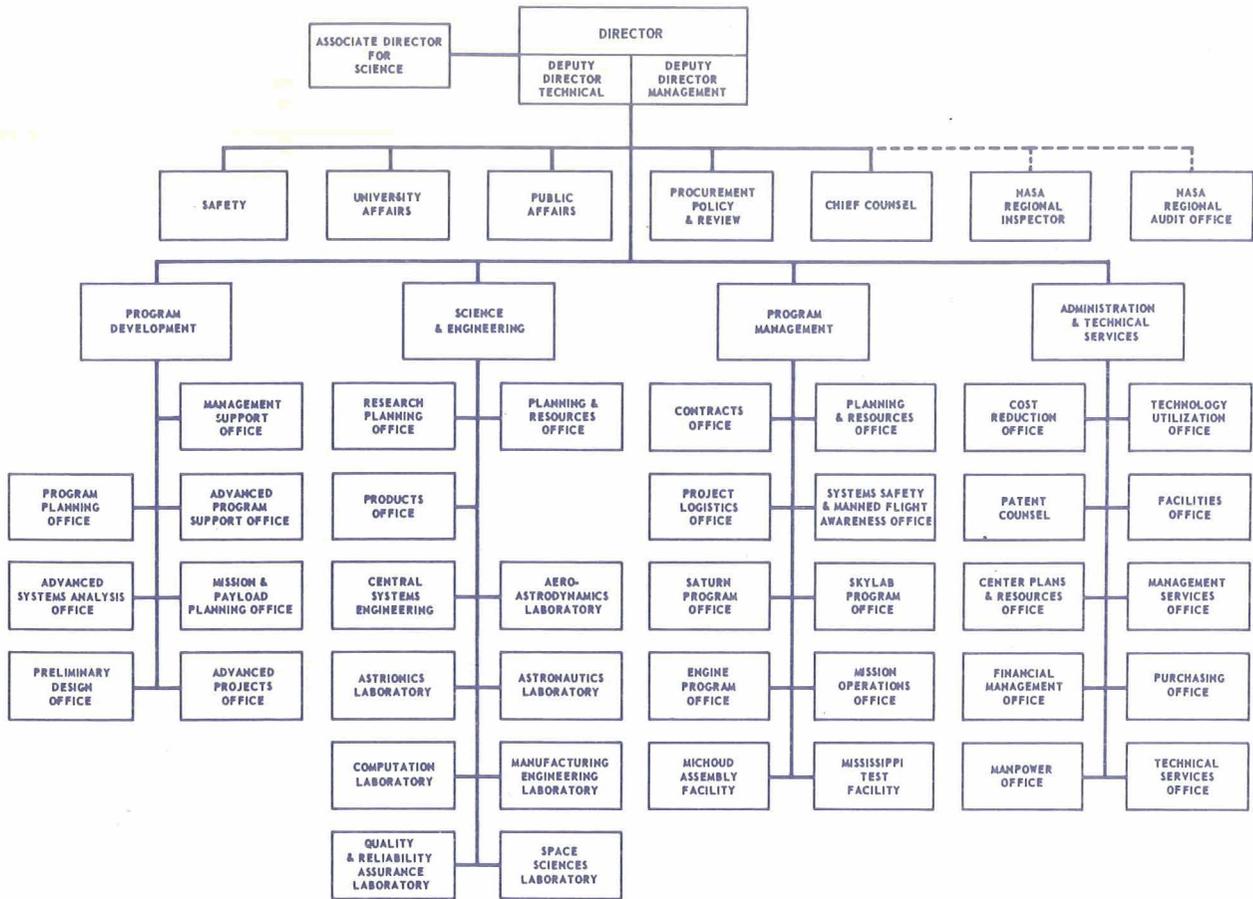
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MATERIALS RESEARCH FOR SHUTTLE AND SPACE STATION

RESEARCH ACHIEVEMENTS REVIEW
VOLUME III REPORT NO. 10

SCIENCE AND ENGINEERING DIRECTORATE
GEORGE C. MARSHALL SPACE FLIGHT CENTER
MARSHALL SPACE FLIGHT CENTER, ALABAMA

GEORGE C. MARSHALL SPACE FLIGHT CENTER



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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON, D. C.

RESEARCH ACHIEVEMENTS REVIEW
VOLUME III **REPORT NO.10**

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PREFACE

In February, 1965, Dr. Ernst Stuhlinger, now Marshall Space Flight Center's Associate Director for Science, initiated a series of Research Achievements Reviews which set forth those achievements accomplished by the laboratories of the Marshall Space Flight Center. Each review covered one or two fields of research in a form readily usable by specialists, systems engineers and program managers. The review of February 24, 1966, completed this series. Each review was documented in the "Research Achievements Review Series."

In March, 1966, a second series of Research Achievements Reviews was initiated. This second series emphasized research areas of greatest concentration of effort, of most rapid progress, or of most pertinent interest and was published as "Research Achievements Review Reports, Volume II." Volume II covered the reviews from March, 1966, through February, 1968.

This third series of Research Achievements Reviews was begun in March, 1968, and continues the concept introduced in the second series. Reviews of the third series are designated Volume III and will span the period from March, 1968, through March, 1970.

The papers in this report were presented December 18, 1969

William G. Johnson
Director
Research Planning Office

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INTRODUCTION TO MATERIALS RESEARCH FOR SHUTTLE AND SPACE STATION

By

R. J. Schwinghamer

The importance of materials research to flight was pointed out as far back as the days of ancient Greece. In Greek mythology the story of Daedalus and Icarus told how Icarus met his downfall because the wax, which he used to hold the feathers to his arms, melted when he flew too close to the sun. This tale is probably the first recorded reference to a catastrophic materials failure in flight. It may also be the first and most dramatic demonstration of the need for a thermal protection system.

The papers in this Research Achievement Review similarly emphasize the importance of materials to flight — specifically to the NASA Space Station/Base and Space Shuttle programs.

The first paper in this review is concerned with bearings and lubricants in a long term space environment. It is believed that bearings and lubricants for use in the space environment for Space Station and Shuttle application will require further development. In retrospect, it's easy to see how naive everyone really was when the S-3D engine turbo gear froze up and stopped abruptly shortly after launch on U. S. Army Jupiter Missile no. 3. That was probably the first exposure to the practical danger of exceeding the vapor pressure of a lubricant.

In spite of the accumulated experience of Mercury, Gemini, and Apollo, window deposit and outgassing problems still exist. The second paper in this review covering outgassing and offgassing, vacuum deposition and redeposition, and thermal radiation effects strikes at the heart of the window problems and provides essential design data for spacecraft contamination control in general. As a result of the substantial effort to date and future planned activity, Shuttle and Space Station window or optics contamination problems are not expected to continue.

The third subject, the space processing of materials, has an interesting facet that involves

crystal growing in null gravity. This paper attempts to explain what is being done about it terrestrially as a prelude to future Space Station activity.

Unquestionably, in the Shuttle activity, one of the big departures from previous practice will come in the area of nondestructive testing (NDT) of the Shuttle and, probably, the Space Station as well. Reusability, short turnaround times, and limited accessibility will provide the forcing function for integrated, automated NDT. In some cases, the NDT diagnostics are envisioned as a permanent part of the vehicle or station. These new concepts are discussed briefly in this treatment of the subject.

Although nuclear activities in the past have endured a rather spotty support picture, there is decided evidence that nuclear technology is inevitable in Space Station power plant development and highly probable in tug or ferry operations. In spite of the fact that the trend has been away from the nuclear area in the recent past, because of firm convictions along these lines, a fairly healthy nuclear materials technology development program has continued. Continued activity in this area now promises ultimately to provide a rational basis for the selection of insulations, adhesives, seals, and lubricants as well as appreciable insight into the synergistic effects of materials in the nuclear environment.

Currently, it is being discovered that the Shuttle vehicle requires the use of a number of materials that past programs at Marshall Space Flight Center have not involved. Some of these materials, especially in the case of the Shuttle, may have to be used in heretofore untried combinations. At Marshall, a promising way of combining some of these unusual metallurgical combinations is being developed. An account of the unique in-house experiments, using high explosives to bond these materials, is quite fascinating and promising.

One of the hottest metallurgical subjects in the advanced Shuttle development area now is metal matrix composites. The results of scrutiny to date including a couple of relatively new and quite promising materials for use in matrix composites are discussed herein.

Next, a kind of a parvenu phenomenon will be discussed that isn't really understood well enough yet for the total implications to be assessed; i. e. , gaseous hydrogen embrittlement. With goals of 75 to 100 flights per Shuttle, there is extreme concern about the continued exposure of crucial parts to gaseous H_2 . When only a one-shot basis is flown, gaseous H_2 embrittlement may or may not be a problem, but for 100 flights it almost certainly is.

The next subject, fuel tank sealants, may or may not be pertinent to Shuttle design. If the air breathers turn out to be H_2 air breathers, fuel tank sealants of the type being developed for the SST may not play much of a role in Shuttle development.

However, one can never be sure at this stage of the game, so this sealant research work may have an even earlier payoff than was originally anticipated.

Along similar lines, but perhaps more basic in nature is the work at Marshall in synthesizing a new series of fluorinated aromatic diamines and diisocyanates. This work is believed to have promise for the future. This vanguard effort is discussed briefly.

The last subject, but by no means the least important subject, has to do with that much discussed subject, flammability. The testing, evaluation, and improvement of materials for use in spacecraft habitable areas is an activity that constitutes a fairly large segment of the Materials Division activity. This is probably one of the most misunderstood of all the subjects contained in this review. This discussion will attempt to provide some new insight into this problem as it pertains to the Shuttle and Space Station.

BEARING AND LUBRICANT RESEARCH FOR SHUTTLE TYPE SPACECRAFT

By

K. E. Demorest

INTRODUCTION

The development of a Shuttle spacecraft will require mechanisms that operate in space, during reentry, and in earth-ambient environments. Any of these mechanisms that have moving parts will require some form of lubrication, and all lubricants are affected in some manner by the environment in which they are required to operate. The environments anticipated for a Shuttle spacecraft and their effect on lubrication are shown in Table 1. Certainly these environments are not unique to this phase of the space program; however, the multiple reuse requirement and the associated cycling from one type of environment to another present unusual problems.

DISCUSSION

To introduce a discussion of Space Shuttle lubrication problems let us first consider several

statements that are true for all mechanical design:

1. All mechanisms that have contacting elements in relative motion to each other require some form of lubrication.
2. The purpose of a lubricant is to reduce friction, prevent wear or damage to the contacting surfaces, and to remove heat.
3. Two general classes of lubricants are in use today, these being categorized as fluid and dry. A list of the advantages and disadvantages of each class is shown in Table 2.

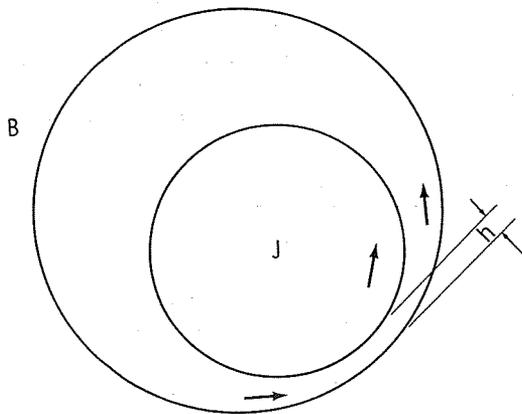
The major advantage of fluid lubricants is their ability to form a hydrodynamic film as illustrated by the schematic of a journal bearing in Figure 1. As the journal (*J*) in the schematic rotates in the bearing (*B*), fluid in the clearance between the journal and bearing is pumped into the area under the bearing load to form a load supporting film having a thickness (*h*). The thickness or height of this film is a function of the fluid viscosity and bearing speed

TABLE 1. ANTICIPATED SHUTTLE ENVIRONMENTS

<u>Space Operation</u>	<u>Environment</u>	<u>Effects</u>
	Vacuum	Loss of Lubricant Because of Outgassing
	Low Temperature	Freezing of Fluid Lubricants
	High Temperature	Loss of Lubricant; Reduced Viscosity
<u>Reentry</u>	<u>Environment</u>	<u>Effects</u>
	Very High Temperature	Loss of Lubricant; Oxidation of Lubricant
	Air	Corrosion of Machine Elements

TABLE 2. ADVANTAGES AND DISADVANTAGES OF LUBRICANTS

Fluids
<ol style="list-style-type: none"> 1. Hydrodynamic Film Provides Low Friction and Long Wear Life 2. Good Cooling Characteristics 3. Poor Temperature Range 4. Viscosity Varies With Temperature 5. Complex System
Dry (Solids)
<ol style="list-style-type: none"> 1. Good Load Carrying Ability at Low Speeds 2. Simple System 3. Good Temperature Range 4. Boundary Lubrication Gives Poor Wear Life and High Friction 5. Poor Cooling Characteristics



$$h = f \frac{S\mu}{W}$$

WHERE h = FILM THICKNESS

S = SPEED

μ = VISCOSITY

W = LOAD

Figure 1. Journal bearing schematic.

and is an inverse function of the load applied to the bearing. When the film (h) is sufficiently thick to prevent contact of surface asperities between the journal and the bearing, full hydrodynamic lubrication exists and the friction of the bearing is a function of the shear strength of the fluid film. This condition is ideal since almost no wear occurs between the bearing and the journal.

The ability of fluid lubricants to form a hydrodynamic film and their excellent heat transfer characteristics are offset by the rather narrow liquid range with respect to temperature of most fluids, their relatively high vapor pressure, and their wide viscosity range. Most fluids tend to outgas badly in vacuum especially at fairly high temperatures. The effect of temperature on the torque and the vacuum weight loss of Krytox 240 AB, one of the better vacuum greases, is shown in Figure 2.

Even when fluids are operating between their freezing and boiling points, their viscosity and, therefore, their ability to form a hydrodynamic film varies widely with temperature. This variation in viscosity with temperature is illustrated for several types of fluid lubricants in Figure 3.

Dry, or solid, lubricants work by providing low shear conditions between the lubricated surfaces. Such materials as MoS₂ provide excellent load carrying capabilities when applied to hard substrates, yet shear rather easily in the direction of relative motion. The generally accepted coefficient of friction of MoS₂ varies from 0.2 at light loads to 0.04 at heavy loads.

The use of solid or dry lubricants allows for a much wider temperature range and presents less problems with vacuum outgassing. The major problems with the dry lubricants are their comparatively short wear life and their inability to remove heat from the lubricated surfaces.

There is a wide variety of solid lubricants available to the design engineer. These include the layer laminar materials such as molybdenum disulfide and graphite. These materials can be applied to a surface as a powder or can be bonded to a surface by either organic or inorganic resins. The plastics such as Teflon, nylon, and polyimide are good lubricants under certain load and speed conditions. The layer laminar materials can be mixed with various metals and compacted at high temperature and pressure to form load carrying solids that can then be machined into bearings and gears. Soft metal films can be applied to hard substrates to provide lubrication over extreme temperature ranges

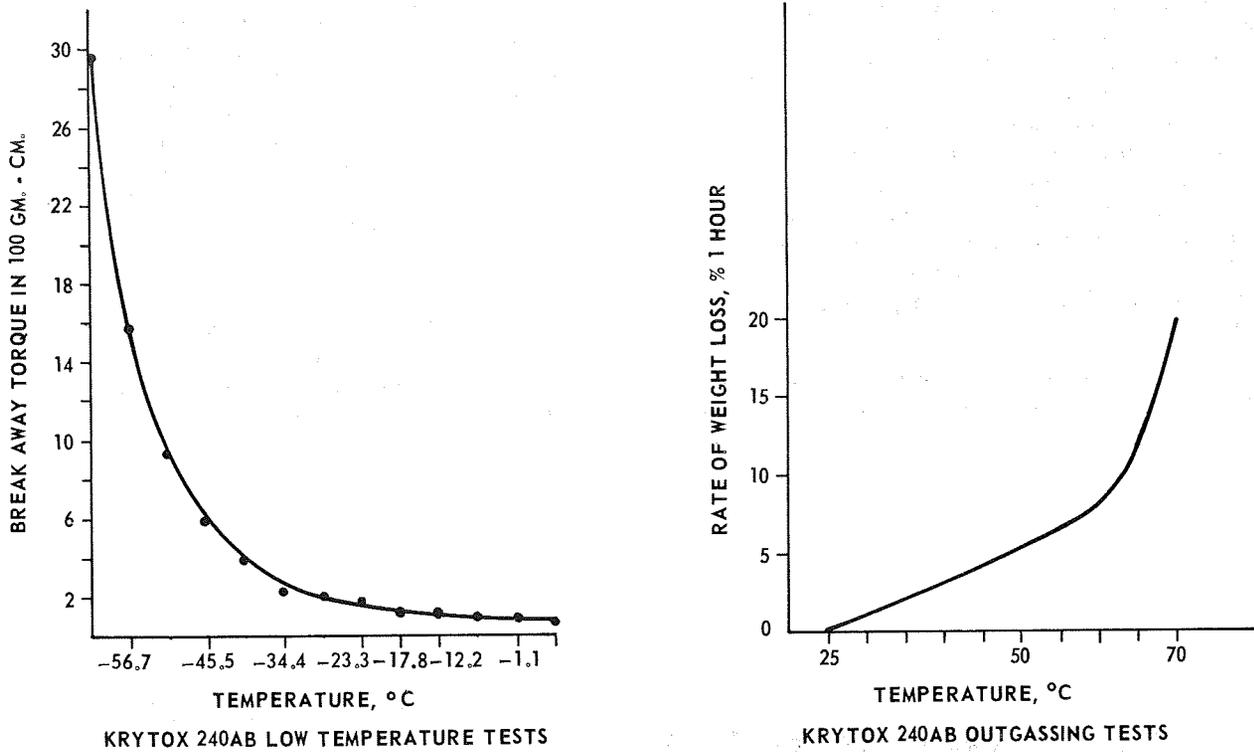


Figure 2. Temperature versus torque and weight loss plots.

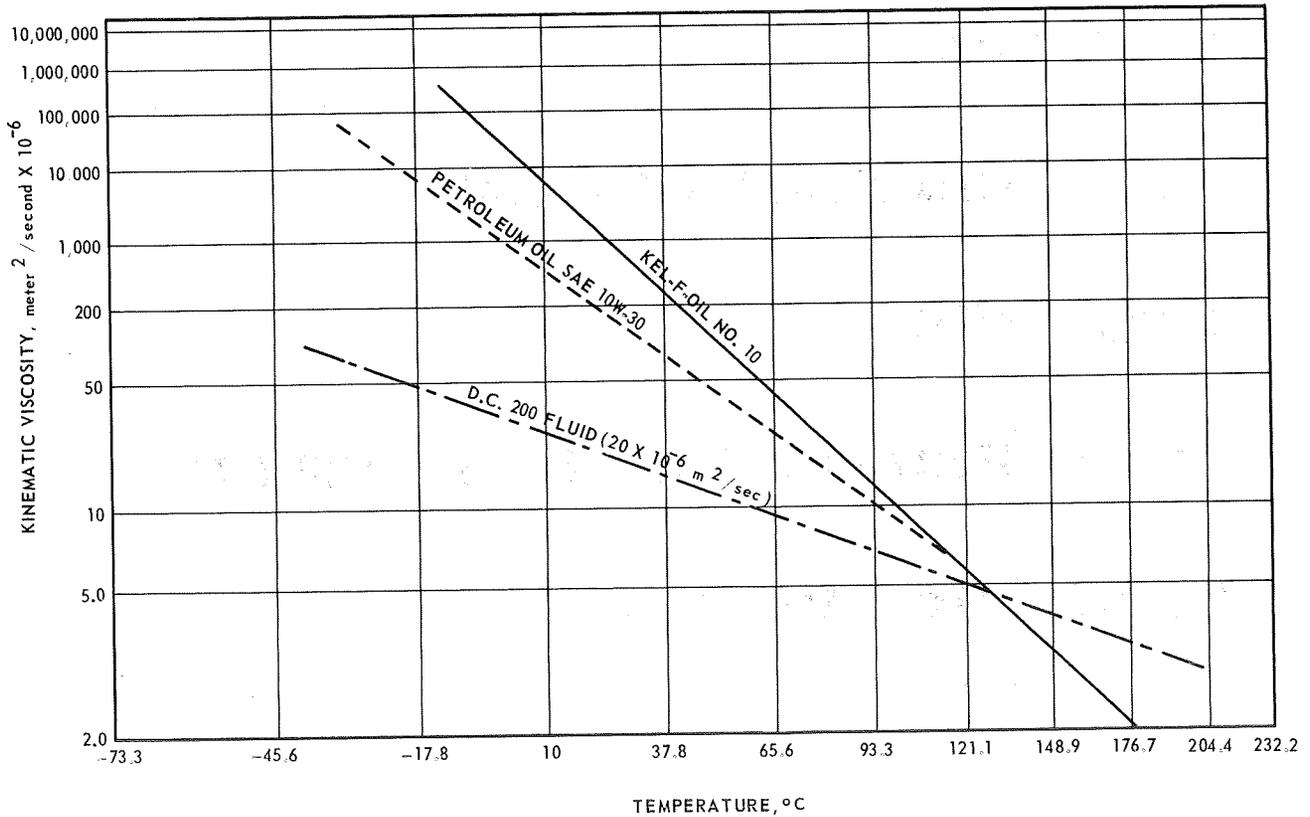


Figure 3. Temperature versus viscosity plots.

As mentioned previously, the limited wear life of the dry lubricants tends to restrict their use. However, during the past few years, developments in this field have increased the wear life and, therefore, the usefulness of these materials many fold. An example of these developments is shown in Figure 4. The Falex Tests shown are standard tests used in a number of specifications. A 1-hour wear life on this machine was considered very good a decade ago. Today at least two films exceed this wear life by a factor of 8 to 12 times. This type of developmental work is continuing.

The development of a Shuttle spacecraft will call for major advances in both fluid and dry (solid)

lubrication. Some of these requirements are listed in Table 3. The last item listed is of particular interest. Most machine elements are designed for use with fluid lubrication. It is believed that machine elements specifically designed to use the advantages of solid lubricants may solve some of the vacuum thermal problems being encountered on present spacecraft in addition to those anticipated on the Shuttle spacecraft.

Table 4 lists some of the programs that have been completed or are underway at Marshall Space Flight Center which should have direct application to the Shuttle spacecraft program.

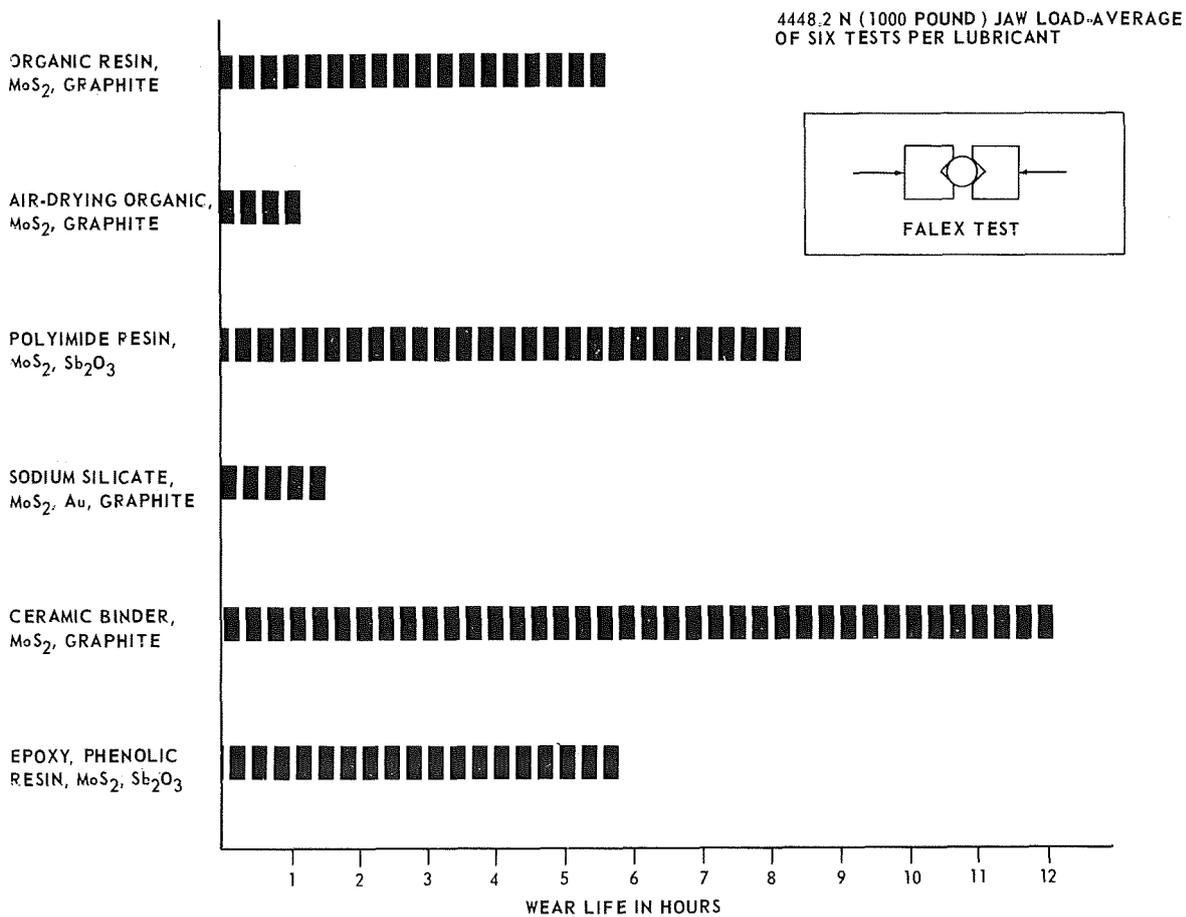


Figure 4. Solid lubricant wear life data.

TABLE 3. ADVANCES NEEDED FOR SHUTTLE AND SPACE STATION LUBRICATION

Fluids
<ol style="list-style-type: none"> 1. Improve Vacuum Thermal Stability 2. Improve Viscosity Curve 3. Improve Corrosion Protection 4. Improve Oxidative Stability 5. Increase Low Temperature Limit
Dry (Solids)
<ol style="list-style-type: none"> 1. Improve Wear Life 2. Reduce Friction Coefficient 3. Improve Thermal Transfer Characteristics 4. Increase High Temperature Limits
General
Design Machine Elements Specifically for Use with Solid Lubricants

SUMMARY AND CONCLUSIONS

The development of a Shuttle type spacecraft will require the use of lubrication systems capable of providing long lives to mechanical components operating across a wide range of environments. These environments will include vacuum and oxidizing atmospheres as well as high and low temperature extremes. A considerable amount of advanced technology development in both fluid and solid lubrication will be required to develop the materials and to supply reliable design data for use in the Shuttle system.

TABLE 4. MSFC LUBRICATION PROGRAMS

<ul style="list-style-type: none"> ● Adhesion of Metals in Vacuum — Complete ● Lubricants for Cryogenic Bearings — Complete ● Ultrahigh Load Lubricants — Complete ● Solid Lubricants for Oscillating Ball Bearings — Complete Development of Dry Lubricants for Use in Ultrahigh Vacuum — In Process ● Radiation Effects on Solid Lubricants — Complete ● Dry Lubricated High Load Bearings for Use in Vacuum — Complete Dry Lubricated Gears — In Process Development of Fluid Lubricants for Use in Space and Radiation Environments — Starting ● Development of Motor Brush Materials for Use in Space — Complete Design of Machine Elements for Use with Dry Lubricants

THERMAL-RADIATION-VACUUM MATERIALS INVESTIGATIONS FOR LONG LIFE ORBITAL SYSTEMS

By

J. C. Horton

SUMMARY

A discussion of the problems involved with materials operating in the environment of space is presented. A brief description of the basic processes of materials' outgassing and the consequences on material properties is given. Methods of utilizing data gained from previous programs are also given.

The several experimental apparatuses and techniques used are described, and the methods of analyzing the data are shown. Several examples on specific materials of information gained from each technique are presented, and their application to long term testing is discussed.

The many problems associated with long term environmental testing are briefly given and the future program in this area is discussed.

INTRODUCTION

The exposure of materials to the harsh environment of space has long been of serious concern to the Materials Division, Astronautics Laboratory of Marshall Space Flight Center. In many programs dating back to 1960, many facets of the complicated interactions of materials with the environment in which they are used have been examined. The effects of pressure, temperature, solar radiation, particulate radiation, and synergistic combinations of these parameters have been determined for a wide variety of different classes of materials. These investigations, however, were always predicted on the basis of a short term exposure to the space environment, and only in a few instances did this exposure result in serious degradation of the material's properties. Effects such as the redeposition of outgas products or surface property changes were of primary concern. Although these problems remain, consideration must now be given

to other physical parameters such as mechanical, electrical, and thermal properties, since it is anticipated that for some materials these parameters will be seriously affected by long duration exposure to the space environment.

BASIC OUTGASSING PROCESS

While relatively little long term environmental testing on materials has been done to date, it is possible to utilize the information that has been obtained. For instance, considerable information is available on the outgassing characteristics of materials in a thermal-vacuum environment. To illustrate how these data can be utilized, consider the four basic outgassing processes listed in Table 1. The first process involves the desorption of surface adsorbed gases (primarily atmospheric) which are either physisorbed or chemisorbed. In the second process molecules that are contained within the bulk of the material, but which are not an integral part of the molecular structure, are evolved from the material. The outgassing of actual parent molecules or significant fragments of the parent molecules occurs in the last process and is indicative of degradation of the basic structure of the material.

TABLE 1. TYPES OF OUTGASSING

- | |
|---|
| <ol style="list-style-type: none">1. Desorption of Surface Adsorbed Gases which are Either:<ol style="list-style-type: none">a. Physisorbedb. Chemisorbed2. Evolvement of Molecules Contained Within the Bulk of the Material but which are not a Part of the Molecular Structure Such as Solvents, Catalysts, and Plasticizers.3. Degradation of Material Fragments of Parent Molecules |
|---|

If outgassing occurs as a result of the first process, it is anticipated that there would be no change in the properties of the material. If outgassing results from the second process, it would not be anticipated that there would be any significant changes in any of the material properties. However, outgassing via the third process obviously would result in serious degradation of most of the properties of the materials.

If analyses of existing outgassing data are made based upon the outgassing mechanisms, it is believed that the behavior of the material under extended space conditions can be predicted. However, to make these analyses, an understanding of the techniques used to obtain outgassing data is necessary. The basic experimental system used by the Materials Division to obtain outgassing data is shown schematically in Figure 1.

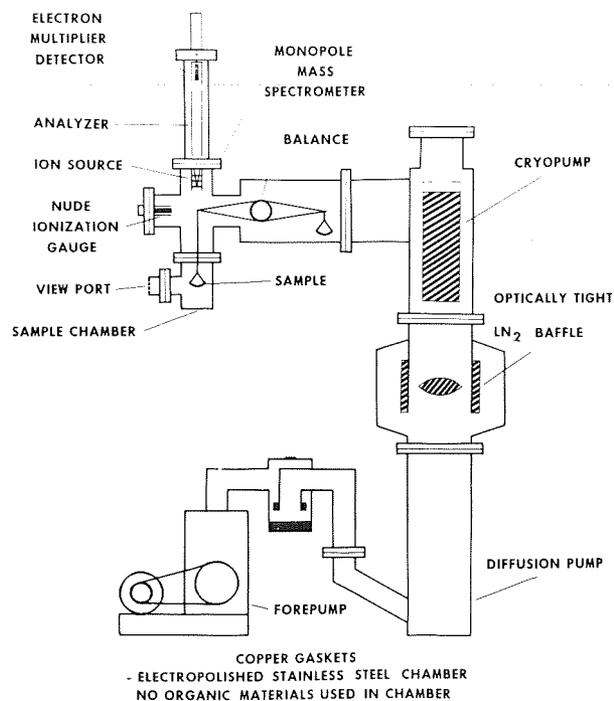


Figure 1. Test apparatus for weight loss and residual gas analysis.

EXPERIMENTAL TECHNIQUE AND ANALYSIS

Very briefly, the experimental technique and analysis system consists of an electropolished stainless steel vacuum system, totally trapped, with a sensitive electrobalance for continuous weight loss measurements and having a nude residual gas analyzer for identifying the outgas products. Figure 2 is a photograph of the system. The use of this equipment permits the identification of the outgassing process responsible for the evolution of the material. With this information, the potential suitability of a material for use in extended orbital missions can be judged. Also, somewhat of a bonus is received by using this technique since the molecules that evolve from the sample can be identified. It is then possible to use this information to modify the basic structure or the processing of the sample to improve its vacuum stability.

Figure 3 is an illustration of the use of this technique. This shows weight loss as a function of both time and temperature for a sample of 2755 Insulcork, a composite material comprised of cork granules with a phenolic binder. This particular material exhibited a rather large weight loss each time the temperature was increased and indicated no tendency to stabilize at a steady-state loss rate. Thus, it obviously is not suited for extended orbital operations. Figure 4 is another example, in this case looking at the data from the residual gas analyzer (RGA). This is a sample of polyurethane foam, specifically the 3D foam for the S-IVB LH₂ tank. This material also exhibited a weight loss, and there was concern that the basic material was being affected. However, both RGA spectra, i. e., at 298.15°K (25°C) and 373.15°K (100°C), clearly indicate the repeating doublet structure at atomic mass units 35, 37, 47, 49, 66, 68, etc., which is attributable to the isotopic ratio of chlorine 35 to chlorine 37. This is the spectrum of trichlorotrifluoromethane (Freon 11), the blowing agent for the foam. This particular type of structure would be expected to lose a small amount of the blowing agent; therefore, the weight loss is not because of a degradation of the basic polyurethane.

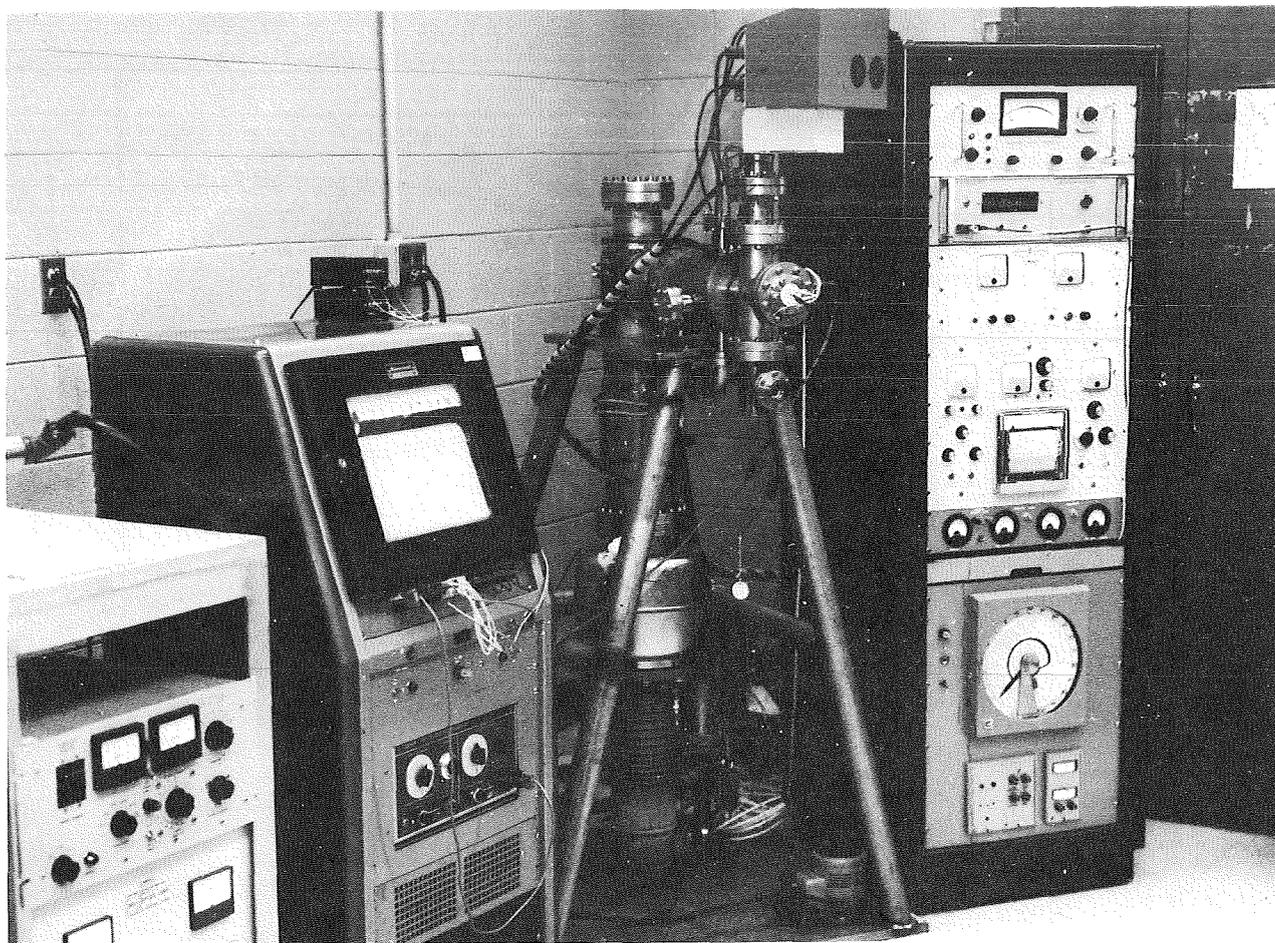


Figure 2. The weight loss and residual gas analysis system.

A second technique is shown schematically in Figure 5. This is a system for determining the thickness of the redeposited outgas products. As molecules evolve from the heated sample, they deposit on the surface of a quartz crystal causing a change in its basic oscillatory frequency. A second crystal adjacent to the first, but shielded from the effluent, is electrically beat against the open crystal, and the resultant beat frequency difference is read out on the associated electronics. This change in frequency resulting from depositing molecules can be interpreted in terms of thickness being deposited. Figure 6 is a closeup view of the two crystal holders in place in the chamber. Shown in Figure 7 is a plot of deposit thickness for cadmium as a function of temperature and time. Cadmium begins depositing about 353, 15°K (80° C) at a very high rate to a total thickness of about 130×10^{-10} m (130 Å). This sample was totally evaporated. Again, this material would not be recommended for long term use in space.

Figure 8 is a similar plot for an organic material, RTV 118. The rate of deposition increases each time the temperature increases and continues to deposit throughout the test. This material also would not be recommended for extended operation in space.

Figure 9 is a photograph of the system used for the third technique, ultraviolet exposure. The sample material is exposed to ultraviolet irradiation from a mercury-xenon source at a 2-sun intensity. The outgassing products are allowed to deposit on a collector disc, either clear quartz or a first surface mirror. The collector disc is then removed and tested to determine the change in optical properties as a function of wavelength. Figure 10 is a plot of optical transmission as a function of wavelength for a sample of Sylgard 182, an optically transparent potting compound. In this case the data were taken from the material itself, since it is transparent.

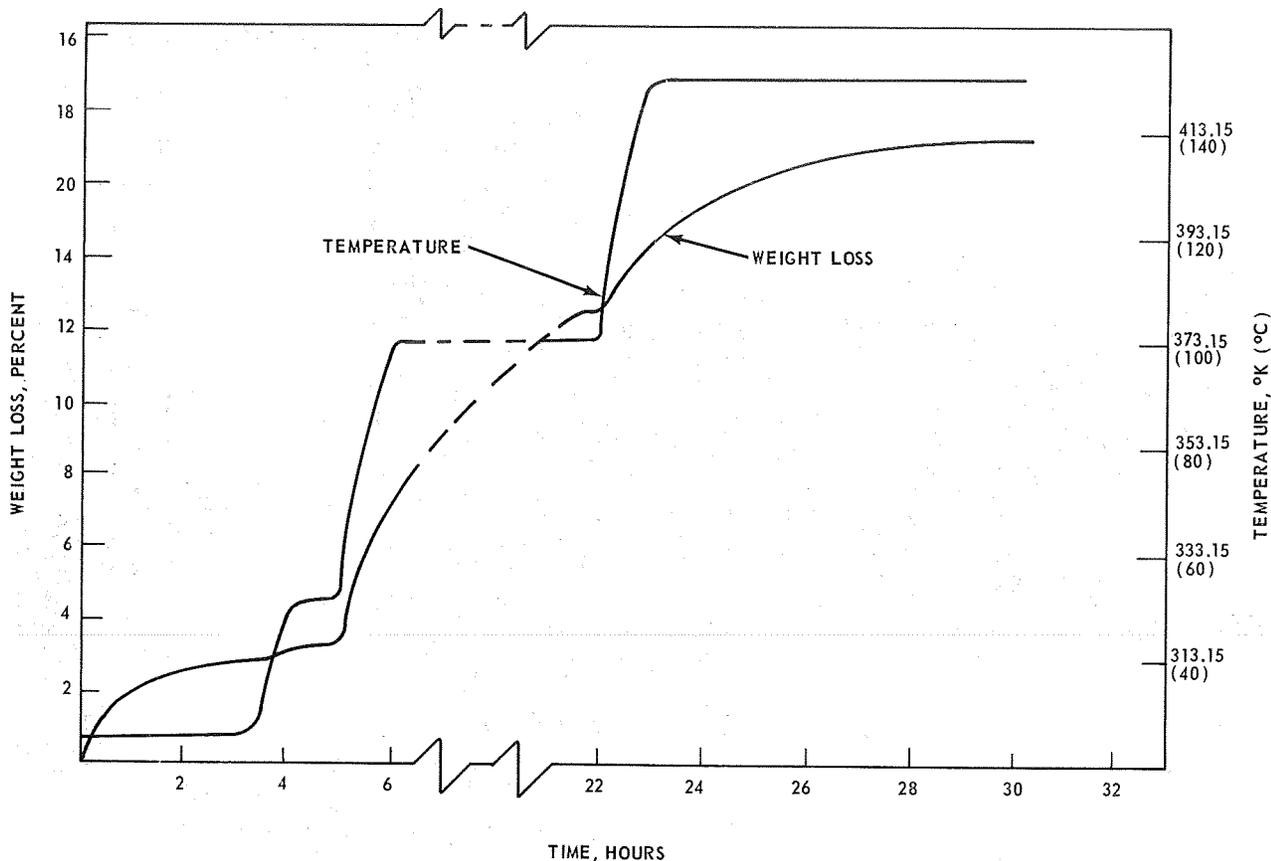


Figure 3. Weight loss of 2755 Insulcork as a function of time and temperature.

Ultraviolet exposure of this material indicates a transmission loss of over 50 percent in the 2500×10^{-10} to 3500×10^{-10} m (2500 to 3500 Å) region. This material would not be suitable unless protected from ultraviolet radiation.

of the samples from the test chamber and exposure to the atmosphere would affect the test results because of the usual absorption and adsorption in the atmosphere. Compounding this is the time required for evaluating one sample, a minimum of about 6 months.

CONCLUSIONS

Using the previous data in this way, a preliminary list of materials as candidates for use on a long-term basis can be produced. Obviously, this does not mean that this material will be satisfactory, but it will eliminate many materials from consideration and reduce the time required to accomplish the task.

The difficulties encountered in long term exposure result from the fact that the materials must be exposed to the space environment and then evaluated while still in that environment. The removal

FUTURE PROGRAM

Two test systems that were designed for conducting long term testing of a large number of samples simultaneously are presently being checked out. This apparatus along with the associated vacuum chambers and environmental simulation equipment will be operational in approximately 3 months. At that time, the long term test program will be initiated. The test program is complex because of the long test time required.

In summary, the materials intended for long term space exposure must be tested, in situ, for their intended use. Previous data generated on other

programs can be utilized to simplify the task. Apparatuses for long term testing, in situ, will be activated in about 3 months.

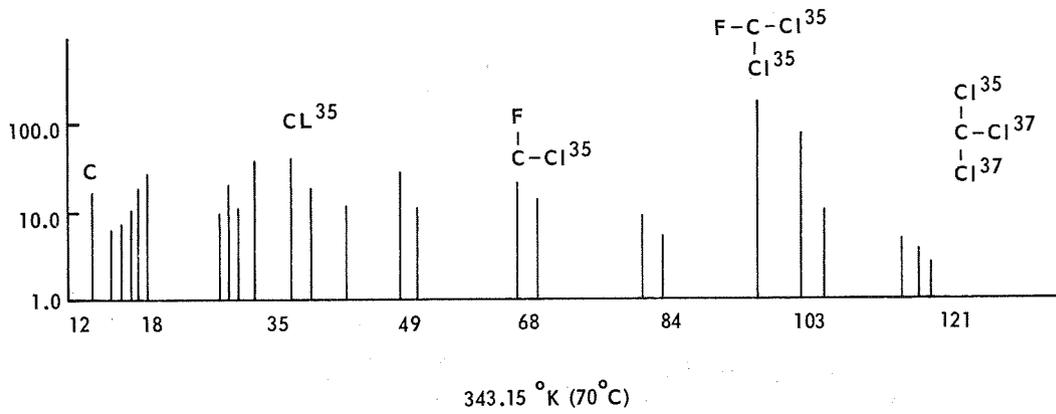
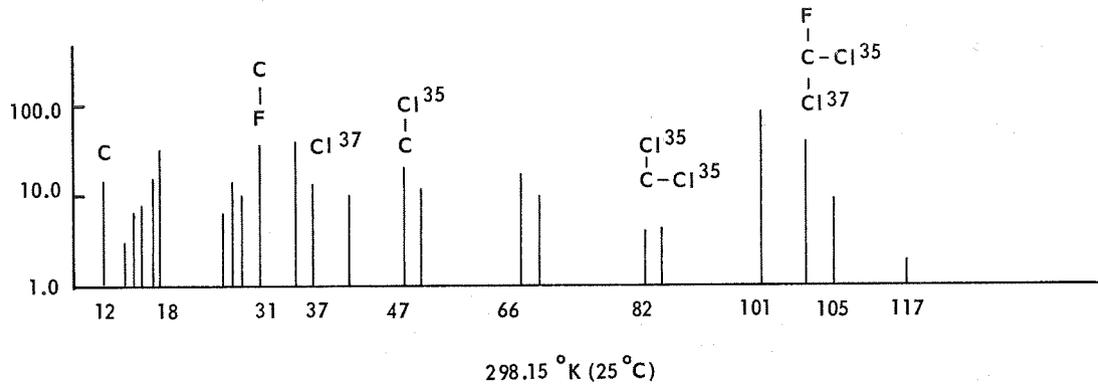


Figure 4. S-IVB tank insulation blown with Freon 11.

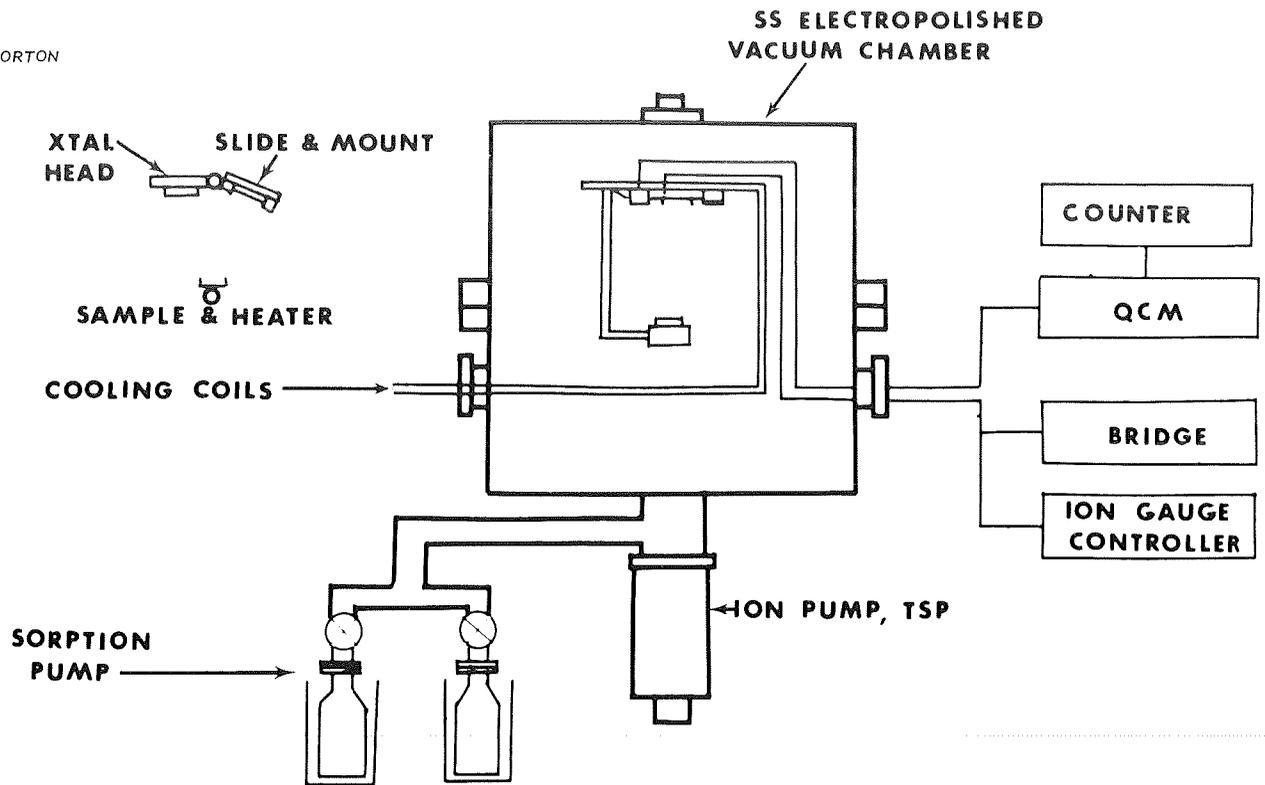


Figure 5. Test apparatus — redeposition.

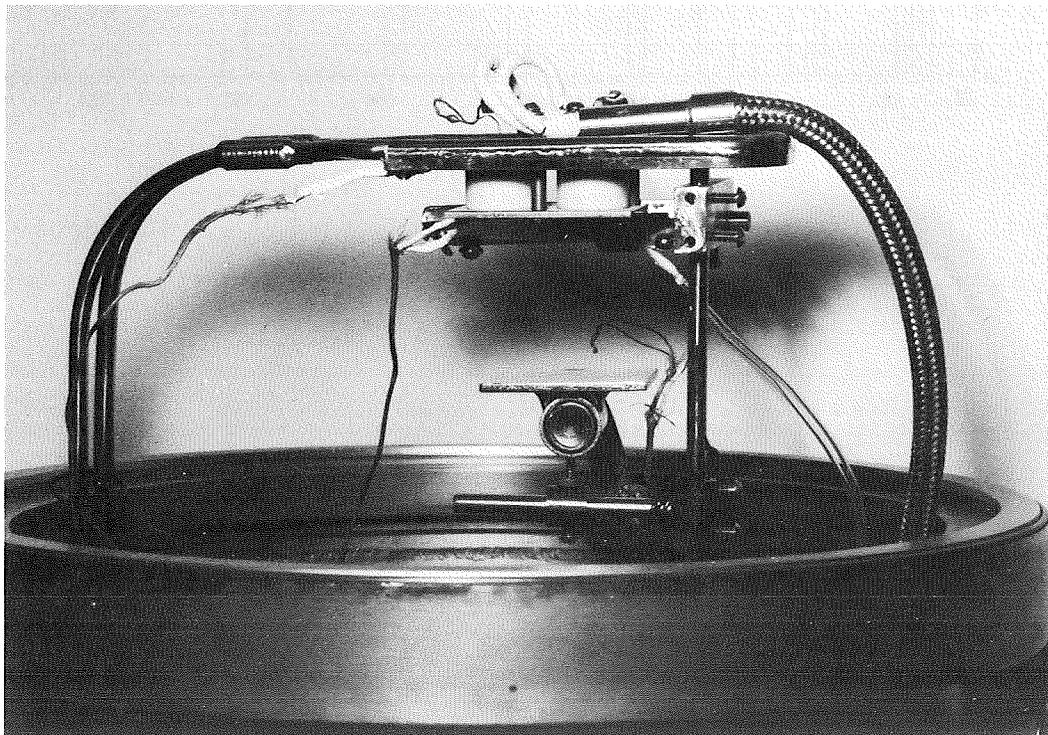


Figure 6. View of the two crystal holders in place in the chamber.

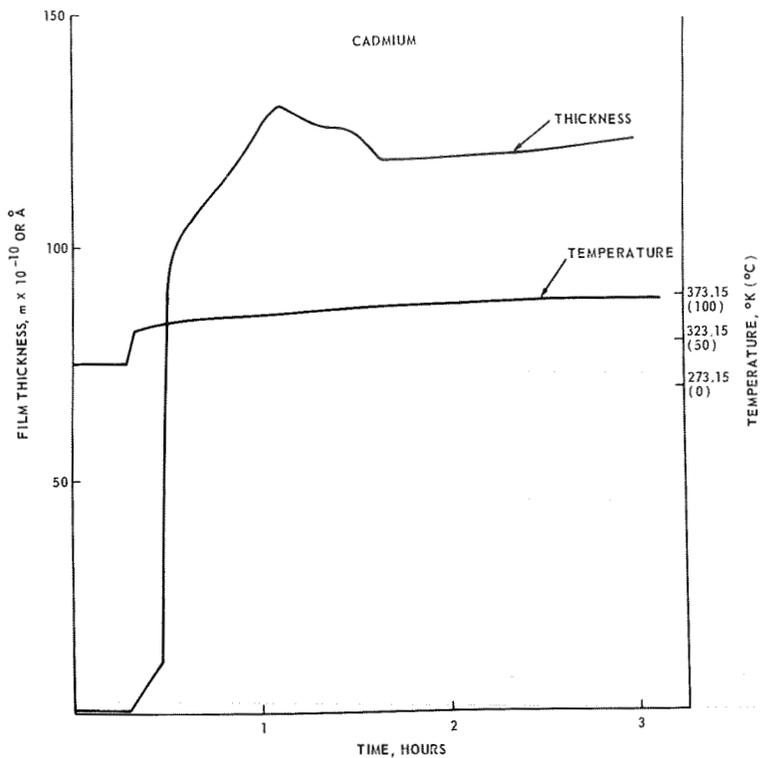


Figure 7. Cadmium film thickness and temperature versus time.

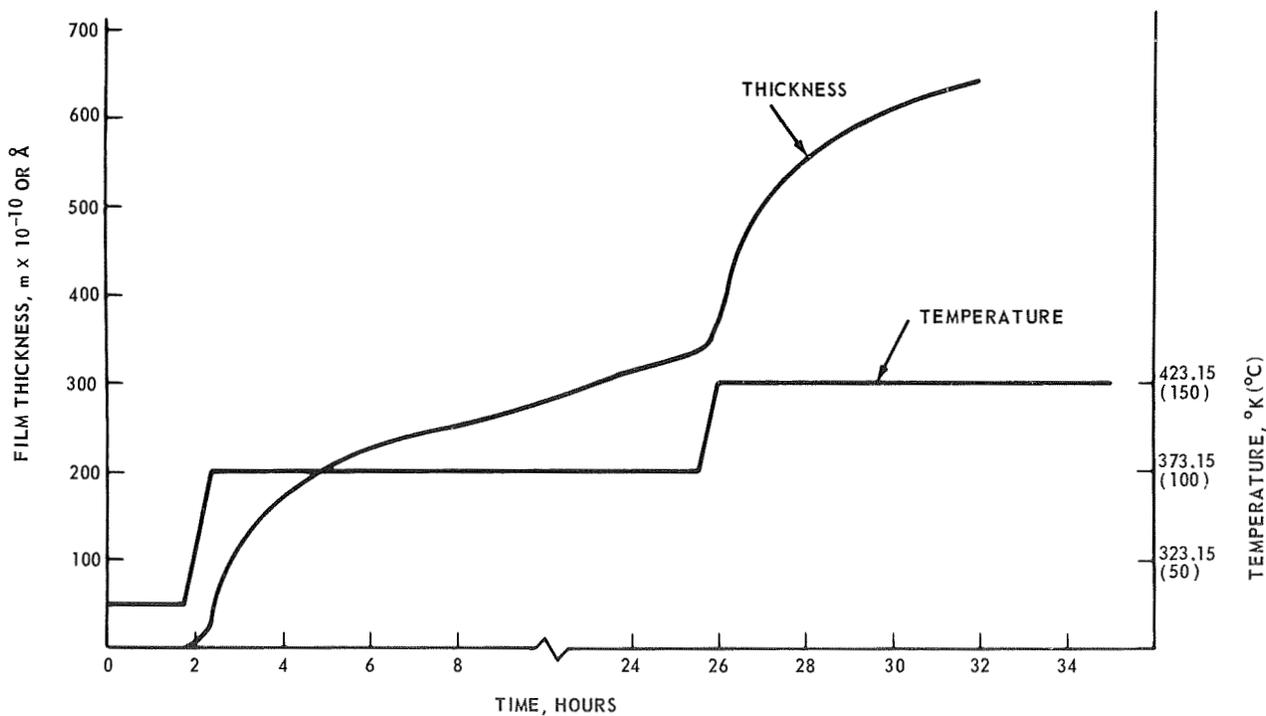


Figure 8. Film thickness and temperature versus time of RTV 118.

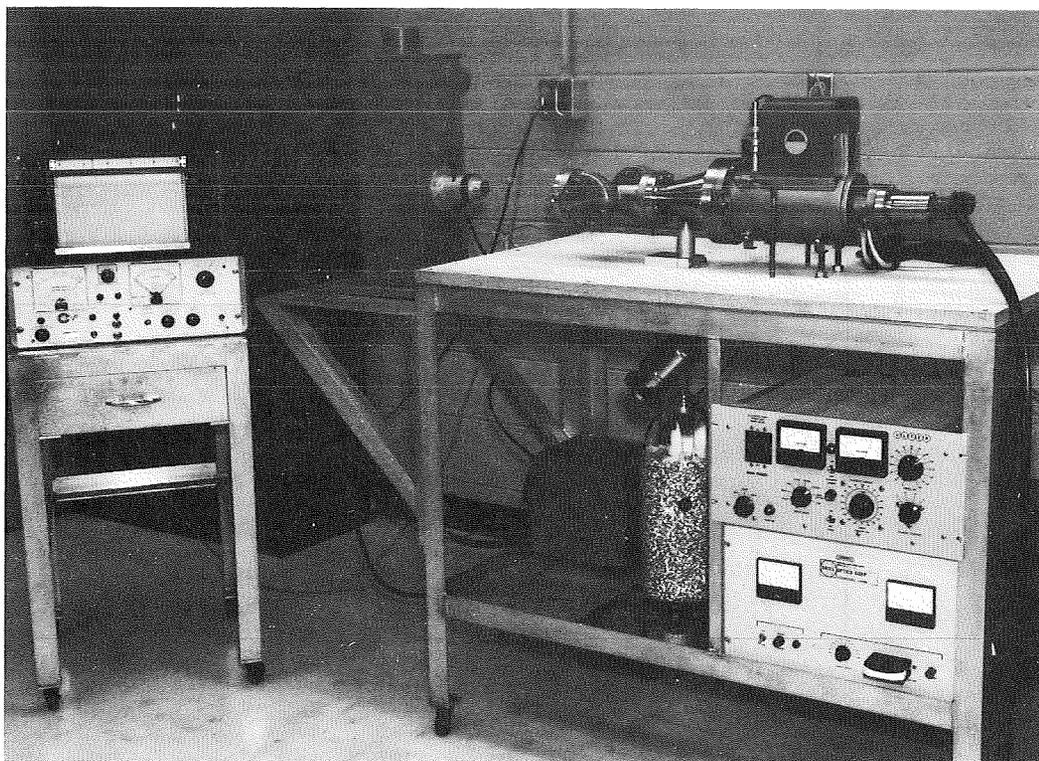


Figure 9. Photograph of the system used for ultraviolet exposure.

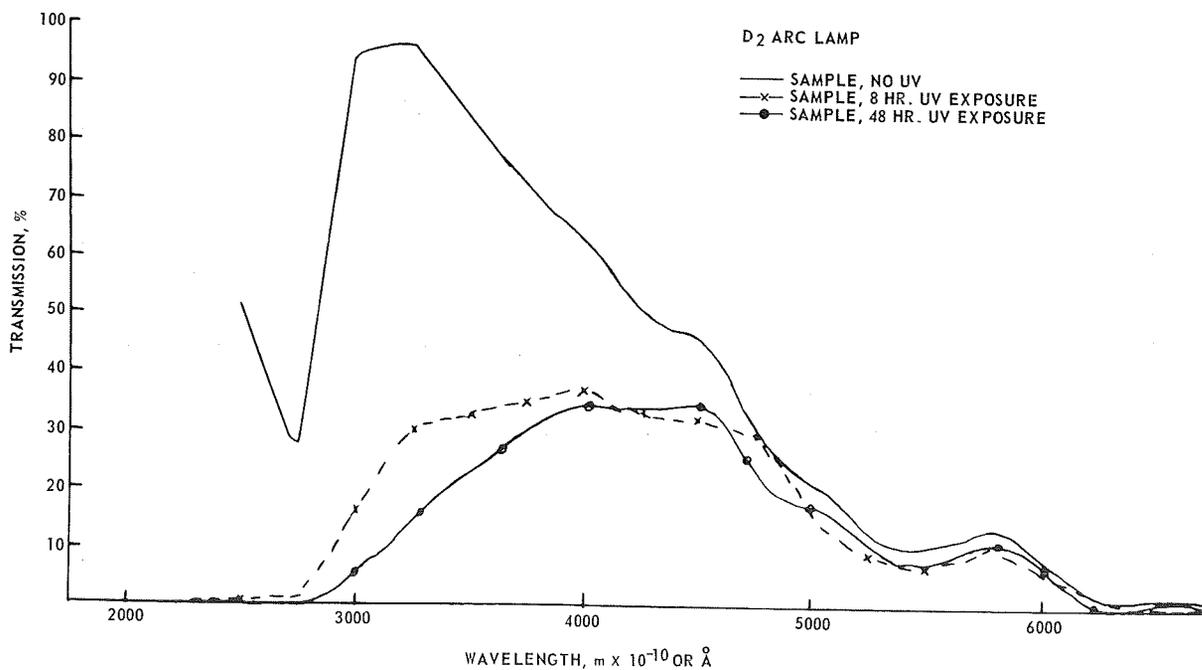


Figure 10. Sample transmission versus wavelength of Sylgard 182.

SPACE PROCESSING OF MATERIALS—TERRESTRIAL PREPARATORY EXPERIMENTS

By

R. C. Ruff

SUMMARY

An introduction to space processing of materials is presented with emphasis on the field of single crystal growth. The introduction includes a discussion of the possible advantages of zero-gravity on crystal growth and the possible effects on crystals grown in zero-gravity. The terrestrial preparatory experiments being performed by the Materials Division, Astronautics Laboratory of Marshall Space Flight Center (MSFC) are discussed from the viewpoint of what can be learned on earth to make experiments in space yield greater dividends. Several specific experiments being performed by the Materials Division are described.

INTRODUCTION

The programs that are presented in this paper deal with space processing of materials with emphasis on crystal growing. The environment of zero-gravity is very intriguing to the solid state physicist. This can be attributed to the fact that crystal growing is a science (or a black art according to some people) that, in many areas, is constrained by gravity. The effects of these constraints are discussed later in this paper. Several space processing experiments are already planned to fly on the Orbital Workshop to study these effects. The terrestrial experiments being performed by the Materials Division of the Astronautics Laboratory of MSFC are designed to prepare the background knowledge necessary to design future experiments for the Materials Research Module.

The possible advantages to crystal growing in zero-gravity are listed in Table 1. It should be emphasized that this is only a preliminary list, and it undoubtedly will be expanded as more work is done

in this area. These advantages are essentially the elimination of the constraints that were mentioned earlier. The macroscopic thermal convection that is such a problem in earth-bound crystal growing techniques is not expected to occur in zero-gravity. This is because in the absence of gravity, there is no buoyancy force between individual volumes of the liquid that are of different density because of differences in temperature. In zero-gravity molecular forces are expected to operate without being influenced by the gravity force. A crucible will not be necessary to contain the melt in zero-gravity. This can result in several advantages. The crystal will not be subjected to mechanical deformation by the crucible; there will be no spurious nuclei on the surface of the crystal because of the crucible-melt interface; and the crystal will not be influenced by impurities that are picked up from the crucible.

TABLE 1. POSSIBLE ADVANTAGES TO
CRYSTAL GROWING IN ZERO-GRAVITY

●	No Thermal Convection
●	Molecular Forces Predominate
●	Crucibles Not Necessary
	No Mechanical Deformation
	No Spurious Nuclei
	No Impurity Pickup

Some of the parameters that may be influenced by making use of the advantages mentioned above are listed in Table 2. On the microscopic level it is expected that the dislocation density will be affected. This is because the dislocation density is affected by impurity concentration, spurious nuclei, and both gravitational and crucible strains. The formation of striations may be affected. Striations,

which are a macroscopic banding or grouping of impurities and/or dislocations, are seen on many crystalline materials grown on earth and are eliminated only by complicated techniques. It is expected that the mechanical strain on crystals grown in zero-gravity will be much less than on earth-grown crystals. It is believed that growing a single crystal in zero-gravity will be easier than on earth. The basis for this belief is that crystal growers must often go to elaborate lengths to isolate the crystal growing apparatus from external influences such as mechanical vibrations. This should be extremely easy in zero-gravity.

TABLE 2. PARAMETERS THAT MAY BE AFFECTED BY GROWING CRYSTALS IN ZERO-GRAVITY

● Dislocation Density (Microscopic)
● Striation Density (Macroscopic)
● Mechanical Strain
● Ease in Growing Single Crystal

Some terrestrial experiments that can provide the theoretical and experimental knowledge necessary to design zero-gravity crystal growing experiments are listed in Table 3. The effect of gravity-force can be studied over a range of gravity-values in a centrifuge. These results may be extrapolated to zero-gravity, and, possibly, compared to crystals grown in a drop tower. Thermal convection can be controlled with thermal gradients, magnetic fields, and baffles. Results of experiments using these three controls can be compared, and a knowledge can be derived of what is to be expected in zero-gravity. Two experimental methods for eliminating the crucible on earth are levitation melting and vertical float zone melting. However, these two methods can be used on earth for only a limited number of metals and semiconductors because of stringent requirements on surface tension and density of the material. To obtain the most information from flight experiments, the crystal materials must be chosen with care. The analytical techniques must be developed for studying the crystals when they are returned from space. These analytical techniques will probably be developed in conjunction with the choosing of optimum crystal materials.

TABLE 3. POSSIBLE PREPARATORY TERRESTRIAL EXPERIMENTS TO PREPARE FOR ZERO-GRAVITY EXPERIMENTS

● Control Gravity-Forces
Centrifuge
Drop Tower
● Control Convection
Thermal Gradients
Magnetic Field
Baffles
● Eliminate Crucible
Levitation Melting
Vertical Float Zone Melting
● Find Optimum Crystal Materials
● Develop Analytical Techniques

Table 4 lists the specific experiments being performed by the Materials Division in support of crystal growing studies for space processing. A centrifuge is being used to grow single crystals at increased gravity-forces. It is hoped that knowing the influence of increased gravity will allow extrapolation to effects at zero-gravity. The Czochralski crystal pulling technique is being used to study the effect of thermal convection controlled by applied thermal gradients. Plans have been made to extend this experiment by controlling the thermal convection with an applied magnetic field. Various candidate materials for space processes are being studied. Magnetostrictive transducer materials are being studied to determine if these materials may be grown larger and/or easier in zero-gravity. Electronic materials such as indium antimonide and gallium arsenide are being studied because of the large commercial benefits any improvements in these materials would provide. Electro-optic materials such as potassium sodium niobate are being studied. Some of the more exotic electro-optic materials are grown only as relatively small crystals because of relative density limitations. It is hoped that growth in zero-gravity will produce larger crystals.

TABLE 4. EXPERIMENTS IN MATERIALS DIVISION IN SUPPORT OF CRYSTAL GROWING STUDIES FOR SPACE PROCESSING

●	Crystal Growing in a Centrifuge
●	Crystal Pulling
	In Controlled Thermal Gradients
	In Controlled Magnetic Fields
●	Studying Candidate Materials
	Magnetostrictive Transducers (Sonar)
	Electronic Materials (InSb, GaAs)
	Electro-Optic Materials (KNaN _b O ₃)
●	Develop Analytic Techniques for Detecting Changes in Crystal Perfection
	X-Ray and Optical Analysis
	Scanning Electron Microscope
	Electron Microprobe
	Electronic Properties
	Magnetic Field
	Low Temperature

The analytical techniques that are being used and improved are also listed in Table 4. Optical and x-ray analyses are being used to study crystals on a microscopic scale. These techniques are being used to study growth direction and crystal structure and perfection. The scanning electron microscope and the electron microprobe are being used to study the macroscopic effects such as crystal growth mechanisms and striations of impurities and dislocations. The electronic properties of the materials are being studied both in magnetic fields and at low temperatures.

DESCRIPTION OF EXPERIMENTS

The first experiment to be described is the centrifuge crystal growing experiment. Figure 1 is an overall view of the centrifuge. The centrifuge

arm in the foreground holds the pivoted canister that contains the crystal growing apparatus. A dc torque motor drives the centrifuge. The multiple lead slip ring at the center of the centrifuge is used for thermocouple outputs and electrical resistance heater inputs. Figure 2 is a schematic diagram of the centrifuge furnace assembly. From the melt outward are the graphite crucible, the electrical heater wires in an insulating shell, thermal insulation, and the aluminum case. At the bottom of the crucible are a thermocouple well and a brass heat sink. The heat sink insures that the material nucleates in the pointed tip of the crucible and grows upward.

The material presently being studied is tin. Tin has several advantages as a preliminary material for this experiment. It has a relatively low melting temperature, and the oxide is not an appreciable problem. Also, tin has been well studied by many investigators. This means that the results gathered from the centrifuge will be easily compared to one-gravity work to determine any differences. Other materials will be studied in the centrifuge in the future. To handle other materials, the furnace assembly is presently being redesigned to provide for higher temperatures and for vacuum and purge gases.

Figure 3 shows two of the tin samples that were grown in the centrifuge. The sample on the right, a single crystal, was grown at four-gravity while the polycrystalline sample on the left resulted from a five-gravity attempt. These samples were chemically etched to bring out any grain boundaries. This photograph illustrates a preliminary result that from one- through four-gravity single crystals of tin are relatively easy to grow; while at five-gravity and higher, growth of single crystals becomes extremely difficult but not impossible. This difficulty cannot yet be assigned to either the apparatus or the tin.

Figure 4 shows the form that striations take in most crystals grown at increased gravity-forces. This is a section of a three-gravity crystal polished and etched to bring out the striations. Several sets of crystals have been grown in the centrifuge from one-gravity to five-gravity and are presently being oriented by x-ray techniques. When the orientation results are returned, the striation directions and spacings will be compared to the gravity-force, growth direction, and crystallographic direction. It is expected that some trends will result that can be extrapolated back to zero-gravity.

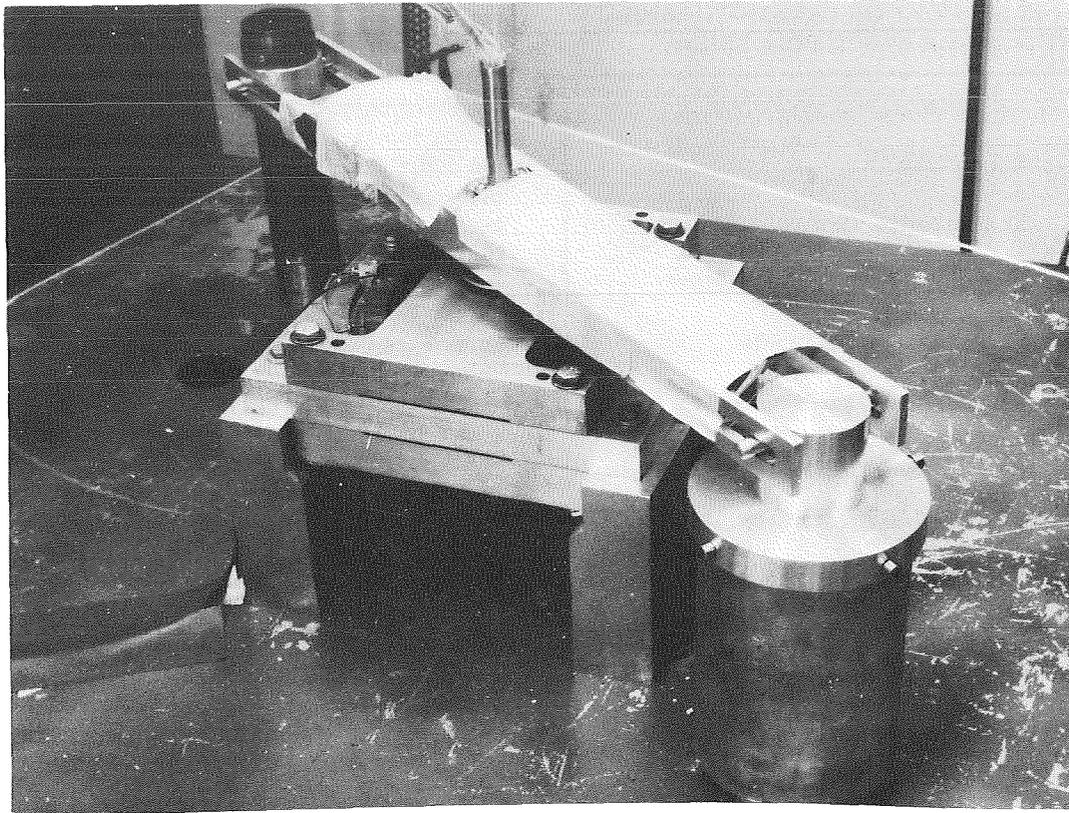


Figure 1. Centrifuge for crystal growing experiments.

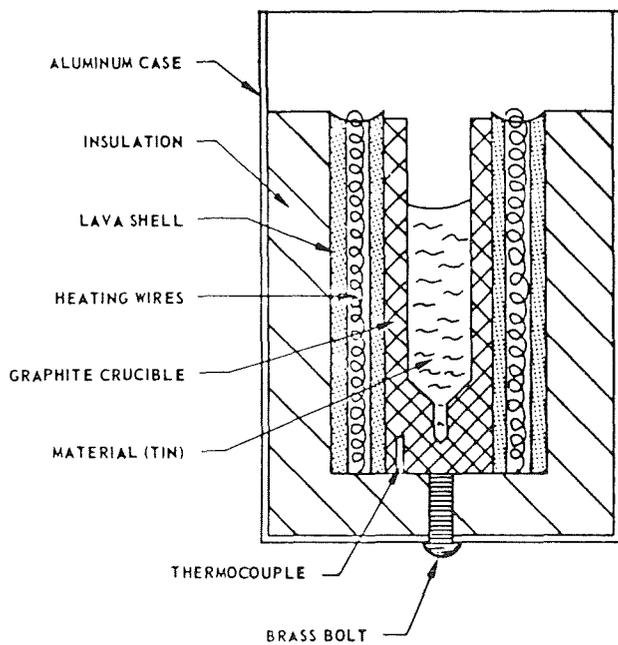


Figure 2. Schematic diagram of centrifuge furnace assembly.

Table 5 lists four of the preliminary results that have been derived from the centrifuge experiment to date. Single crystals can be grown relatively easily from 1-gravity to 5-gravity. The crystal growth mechanism seems to change near 1.5-gravity. Below 1.5-gravity, the crystal growth appears to be of the dendritic type with striation planes intersecting. From 1.5-gravity to 5-gravity, the growth becomes very unidirectional with all striation planes parallel. Last, it can be summarized that increased gravity definitely affects the crystal growth mechanism.

The next experiment to be described is the Czochralski crystal pulling experiment with convection controlled by the thermal gradient. The apparatus for this experiment is shown in Figure 5. The melt is contained in a crucible at the bottom of the sealed quartz tube. The crystal seed is attached to the bottom of a rod that is controlled through the top flange. The equipment provides controlled raising, lowering, and rotation of the seed. The plastic chamber is exhausted by a fan to remove the excess heat and any vapors which may escape.

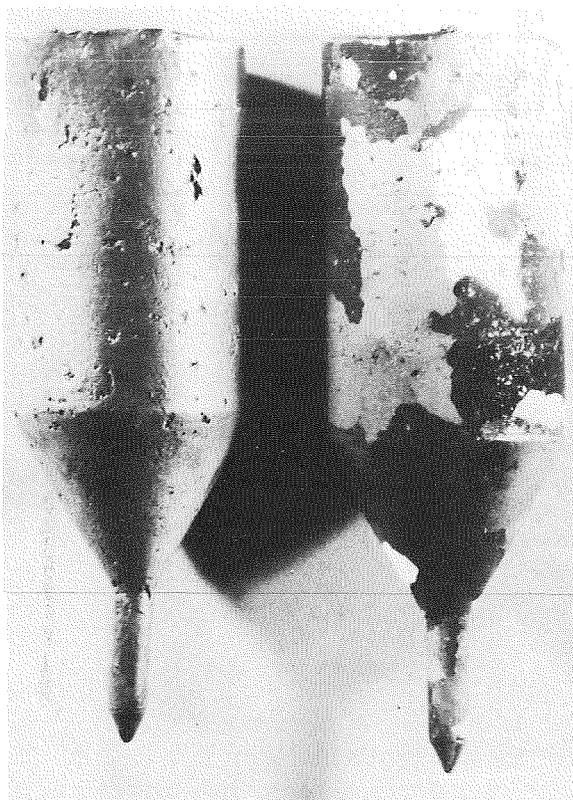


Figure 3. Polycrystal and single crystal tin grown at five-gravity and four-gravity respectively.

Figure 6 is a schematic diagram of the Czochralski crystal pulling apparatus. Shown in Figure 6 are the thermocouples for measuring the temperature gradient on the crucible and the two independent resistance heaters at the top and bottom for controlling the temperature gradient. By controlling the temperature gradient, it is hoped to vary the convection over a wide range and also approach zero-convection. Zero-convection may be an impossibility because the cold seed at the top center of the melt will always disrupt the gradient imposed by the crucible. The melt material that will be studied is indium antimonide. After the crystals are pulled, they will be etched to find any striations or inhomogeneities. The effects or magnitude of the striations will then be related to the convection and an extrapolation made to zero-convection. The zero-convection results will be one possibility of what may happen to crystals grown in zero-gravity.

As an independent approach to zero-convection, it is planned that the same crystal pulling experiments will be performed in a magnetic field. The

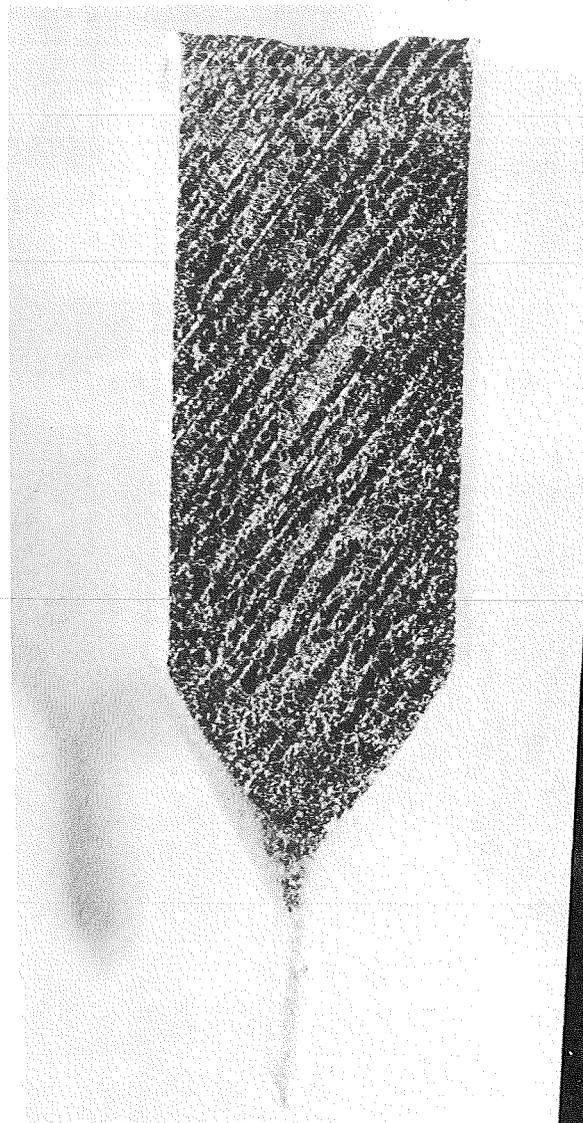


Figure 4. Tin single crystal grown at three-gravity and etched to bring out the striations.

TABLE 5. PRELIMINARY RESULTS FROM CENTRIFUGE EXPERIMENTS

- | | |
|---|---|
| ● | Easily Grown Single Crystals from 1 to 5 Gravity |
| ● | Dendritic Growth from 1 to 1.5 Gravity |
| ● | Unidirectional Dendrite Columns from 1.5 to 5 Gravity |
| ● | Increased Gravity Definitely Affects Crystal Growth |

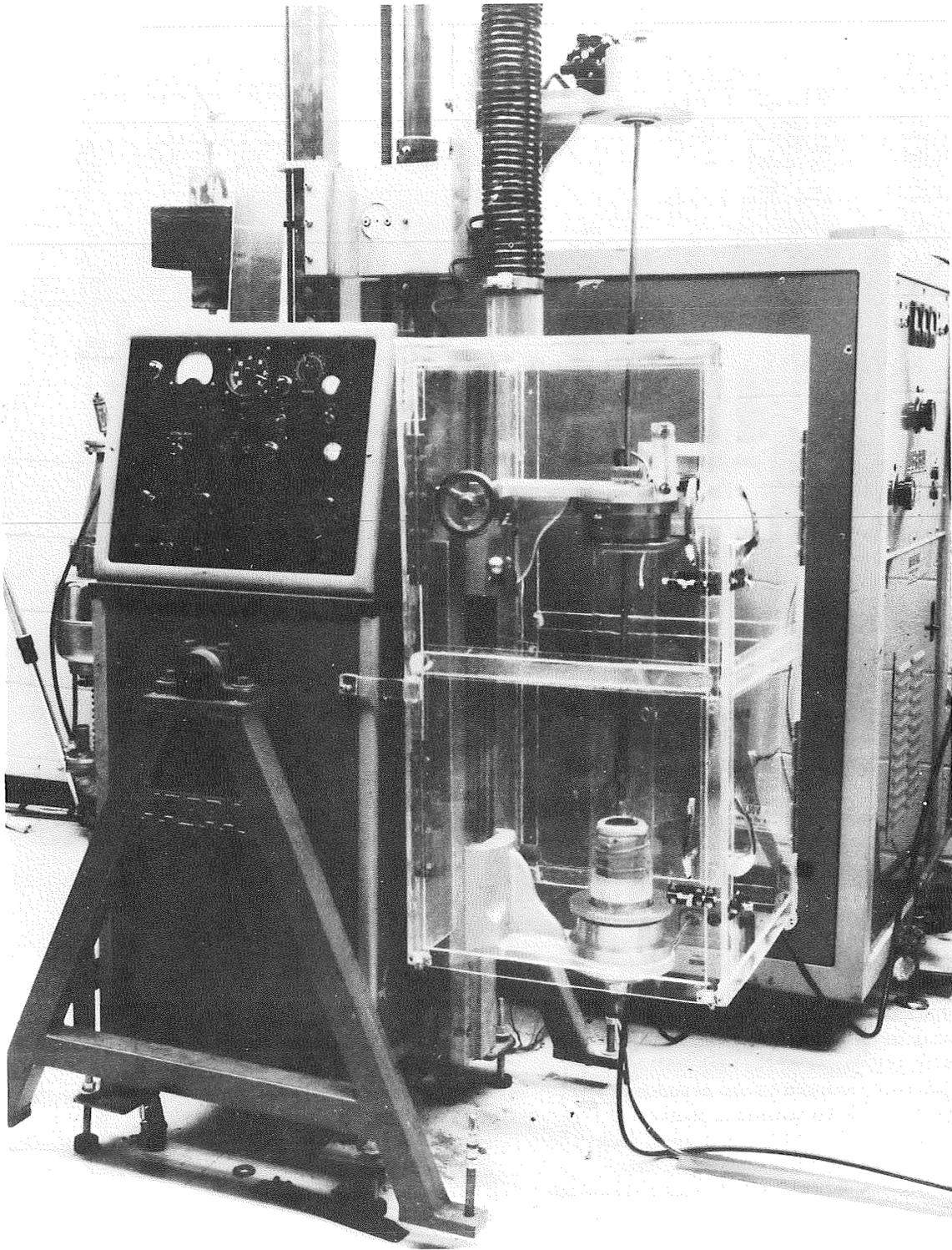


Figure 5. Czochralski crystal pulling apparatus.

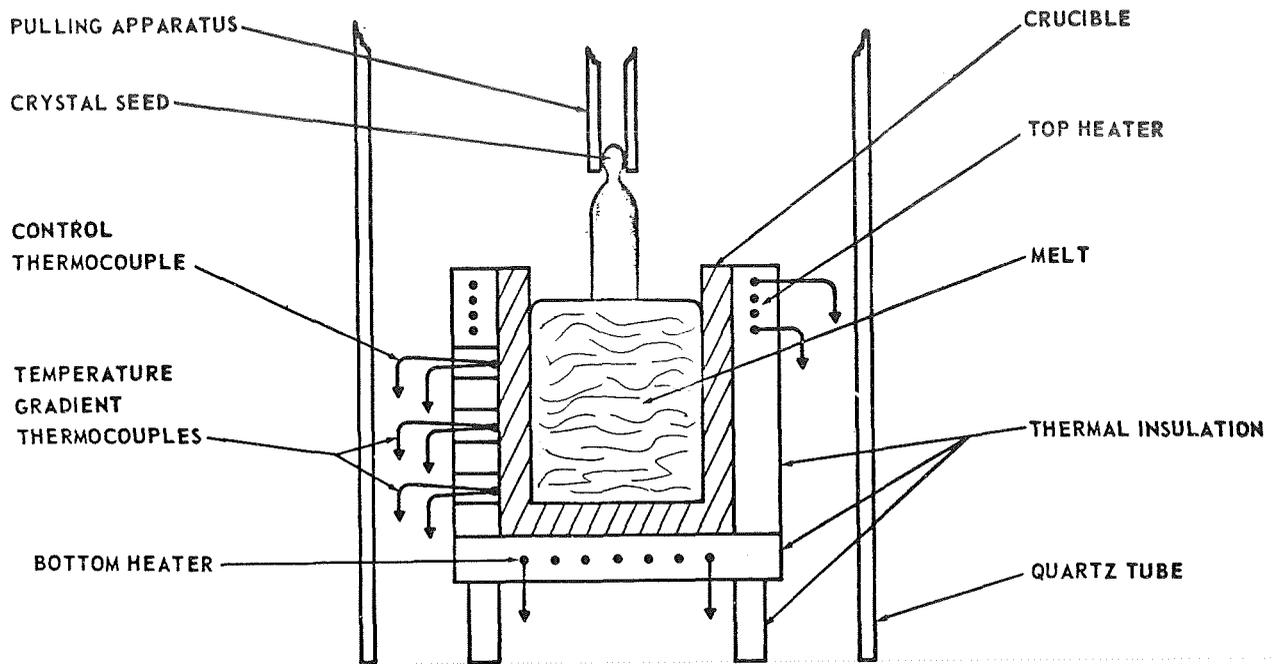


Figure 6. Schematic diagram of Czochralski crystal pulling apparatus.

magnetic field would be used to limit the convection with the possibility of actually realizing zero-convection. This experiment will be a double check on conclusions to be reached from the zero-convection extrapolation from thermal gradients.

In addition to providing much specific information on gravity and convection influences, these three experiments will be extremely useful in providing information that will be helpful in designing future flight experiments. Also, the analytical techniques being developed to study the crystals grown in the laboratory will be necessary to evaluate the crystals grown in space.

CONCLUSIONS

The preparatory experiments of the Materials Division for space processing have several objectives. The centrifuge crystal growing experiment will give direct information on the influence of gravity on crystal growth mechanisms. The Czochralski crystal pulling experiments with convection controlled both by thermal gradients and by magnetic fields will give direct information on the effects to be expected in space with zero-convection. The analytical techniques being developed to study the crystals grown in the laboratory will be applicable to studying crystals brought back from space. With the knowledge of what the major effects in space processing are, the materials for future experiments can more realistically be chosen to yield the most benefits from the experiment.

DEVELOPMENT OF AUTOMATIC NDT SYSTEMS FOR SHUTTLE AND SPACE STATION

By

W. N. Clotfelter

INTRODUCTION

Materials used in the Shuttle will be repeatedly subjected to high stress loads and extreme environmental conditions. The Space Station is to be operational for years. Rigorous and prolonged use of these vehicles adds the complex factor of fatigue to numerous other parameters associated with structural integrity. Materials will require evaluation before being used in these vehicles, critical structural members must be checked during flight, and certain Shuttle components will have to be tested subsequent to every flight. Thus, the need for an effective materials evaluation program is obvious. Onboard instrumentation for automatically monitoring the integrity of structural materials is a major part of this program. Automatic instrumentation is required to: (1) aid the flight crew in making rapid, accurate assessments of structural conditions; (2) monitor inaccessible areas of the craft; and (3) reduce the turnaround time between flights. Principal parameters to be monitored are temperature, thickness of ablative material, integrity of adhesive bonds, fatigue in sheet metal, crack initiation and growth in weldments and forgings, and strain or stress as appropriate in key structural members. Thus, the major objective of this program is the development of automatic diagnostic instrumentation capable of assessing the integrity of critical materials on a continuous basis.

Conventional and new nondestructive evaluation methods can be modified and improved for use in the onboard diagnostic system. This automatic testing, initial materials screening, and supplementary postflight testing will be integrated to form a reliable materials evaluation program.

METHODS OF MONITORING SPACECRAFT MATERIALS

Much well established NDT technology can be applied to the Shuttle and Space Station programs with little difficulty. Useful applications for these conventional testing methods are briefly described under subsequent headings. Recently developed materials evaluation methods are described in greater detail.

TEMPERATURE MEASUREMENTS

Available technology is considered adequate for monitoring temperature. These measurements involve only the location of critical areas of the spacecraft to be monitored, the selection of particular transducer types, and the integration of instrumentation into complete systems. Obviously, this phase of the program must be delayed until exact vehicle configurations are known and material selections are made.

METHODS OF EVALUATING ABLATIVE MATERIAL

Ideally, radiative heat shields should be used on the Shuttle; but since ablative materials will probably be used initially, methods of evaluating them nondestructively are being considered.

Basic electromagnetic and ultrasonic methods suitable for monitoring ablative materials are

available. Microwave techniques are effective for the detection of voids in non-metallic materials. Low frequency electromagnetic or eddy current probes can be used as proximity gages to measure the thickness of ablative heat shields. Probe impedance is affected by its distance from metallic surfaces. Thus, impedance changes can be related to the thickness of material separating the probe from metallic structures. Obviously, electromagnetic instruments used in evaluating ablatives must be applied from the outside of the Shuttle and are considered only for postflight testing.

Resonant or pulse echo ultrasonic techniques of monitoring ablative materials can be made part of an onboard system. However, the optimum technique for each application will be determined by the characteristics of the particular ablative used.

DEBOND DETECTION METHODS

Eddysonic, ultrasonic impedance, ultrasonic attenuation, and thermal techniques are useful for debond detection in many types of composite materials. Eddysonic techniques are most effective when used to evaluate composites having thin metallic face plates. The core material may be metallic or non-metallic. A major advantage of the eddysonic system is that no mechanical contact is required between the transducer and the item being tested. Ultrasonic impedance and surface wave transducers must be coupled to surfaces with a small amount of grease, oil, or water. However, ultrasonic techniques can be used for testing metallic or non-metallic materials. Infrared and the thermal technique utilizing liquid crystals are applicable to debond detection in several types of composite materials. In general, thermal techniques are most effective when all materials used in fabricating the composite have approximately the same value of thermal conductivity.

The debond detection methods discussed are considered primarily for use during the Shuttle turnaround period. However, limited applications of the thermal and ultrasonic methods are considered feasible for onboard testing.

FATIGUE DETECTION METHODS

Several experimenters have used various microwave and ultrasonic techniques to detect very small fatigue cracks in sheet metals. This laboratory instrumentation can be modified for field applications without too much difficulty. However, instrumentation bulk and accessibility problems limit microwave testing to the turnaround period of the Shuttle; but ultrasonic surface wave transducers are simple, inexpensive, and can be easily mounted in selected areas during the manufacturing process. Centrally located readout devices can be used to monitor the transducers that are located in key structural areas.

Resistance fatigue life gages are useful for maintaining a complete stress cycling history of selected surface areas. Minimum instrumentation is required to monitor this gage. Subsequent to adequate calibration, only a simple resistance measurement is necessary to determine the expected useful life remaining in a particular structural component.

METHODS OF MONITORING CRACK INITIATION AND GROWTH

Heavily loaded materials emit sound. In crystalline substances, sound may be caused by the movement of a single dislocation or by the elastic energy released when a crack occurs. Characteristics of this acoustic or stress wave emission can be related to crack growth and to imminent failure of structural materials. Thus, this technology has great potential as an automatic method of monitoring structural integrity.

Cracks occurring in forgings and in welds are the major crack types of interest to MSFC. Preliminary results of in-house and contractual programs are described in this report.

Stress corrosion cracking of the type that occurs in forgings has been simulated by loading beam-type aluminum specimen over an H-frame and subjecting

the material to a corrosive environment. This experimental arrangement is shown in Figure 1. As cracking developed, the sound was detected with a small piezoelectric crystal, amplified, processed, and recorded on a paper chart and on magnetic tape. A microscope was used to monitor obvious cracking and relate it to the occurrence of cracking as indicated by acoustic emission. Figure 2 shows all the experimental apparatus, and Figure 3 depicts typical acoustic emission. Noise generated by specimen insertion and initial chemical action was followed by a quiet period. Initial cracking, as indicated by the emission, occurred in approximately 30 minutes. Cracks were visible with 7X magnification in 1 hour, and complete failure occurred in 2 hours.

Acoustic emission from cracks in welds has been related to indications of a crack opening displacement gage attached to the material and to imminent specimen failure. A block diagram of instrumentation used for this purpose is shown in Figure 4. The basic information is processed through several channels. Real time curves drawn by X-Y recorders speed data evaluation. The tape recordings are used as a "backup" source of information and for detailed analysis. Plots of load versus cumulative emission and load versus cracking opening are shown in Figure 5. The rapid change in the rate of stress wave emission correlates well with the initiation of the nonlinear portion of the crack opening displacement. A comparison of the emission from material containing a flaw to that from unflawed material is

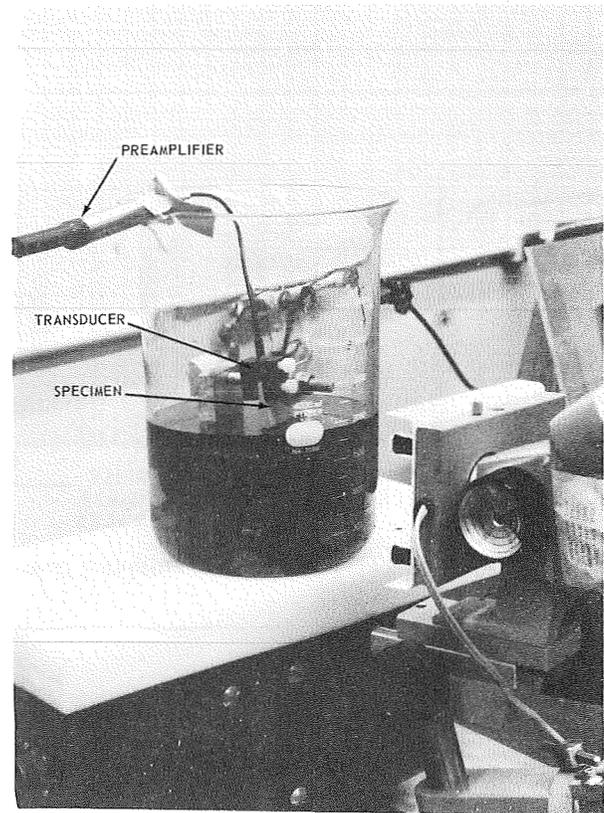


Figure 1. An arrangement used to induce and monitor stress corrosion cracking.

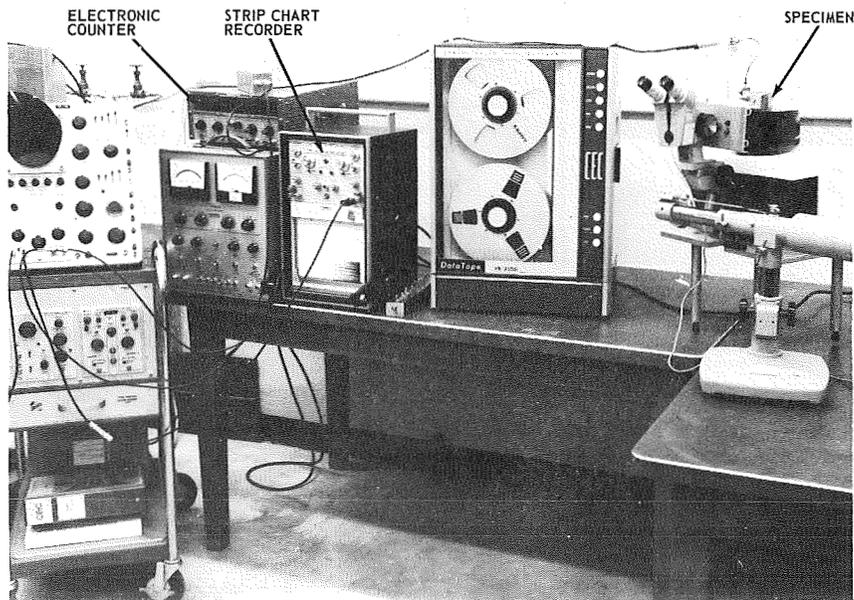


Figure 2. Instrumentation used to monitor stress corrosion cracking.

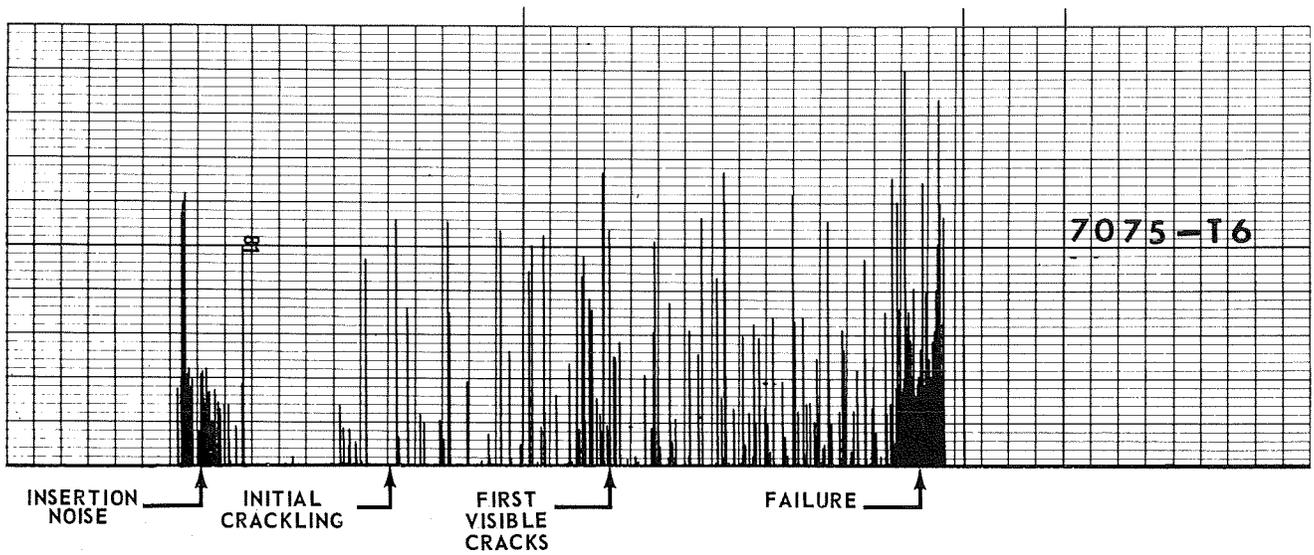


Figure 3. Typical acoustic emission generated by stress corrosion of 7075-T6 aluminum.

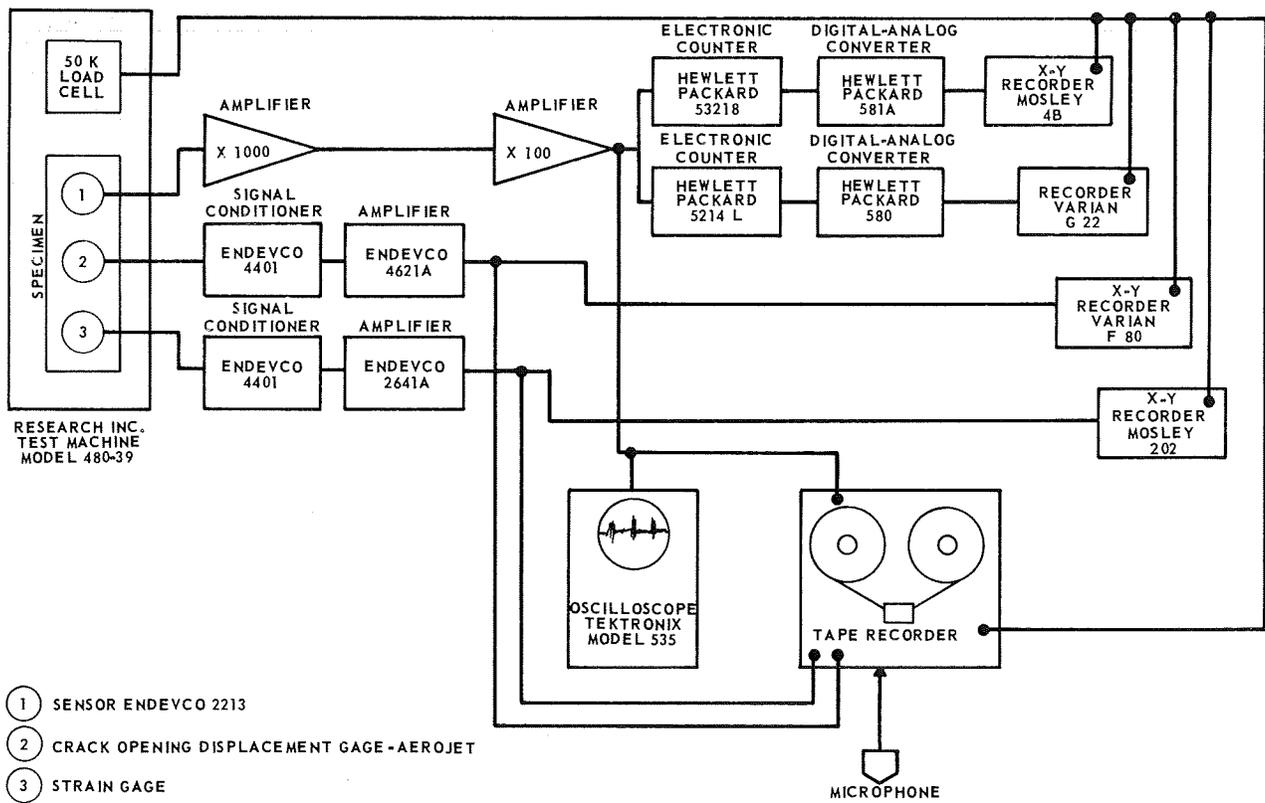


Figure 4. Block diagram of instrumentation used to monitor stress wave emission from crack growth in welds.

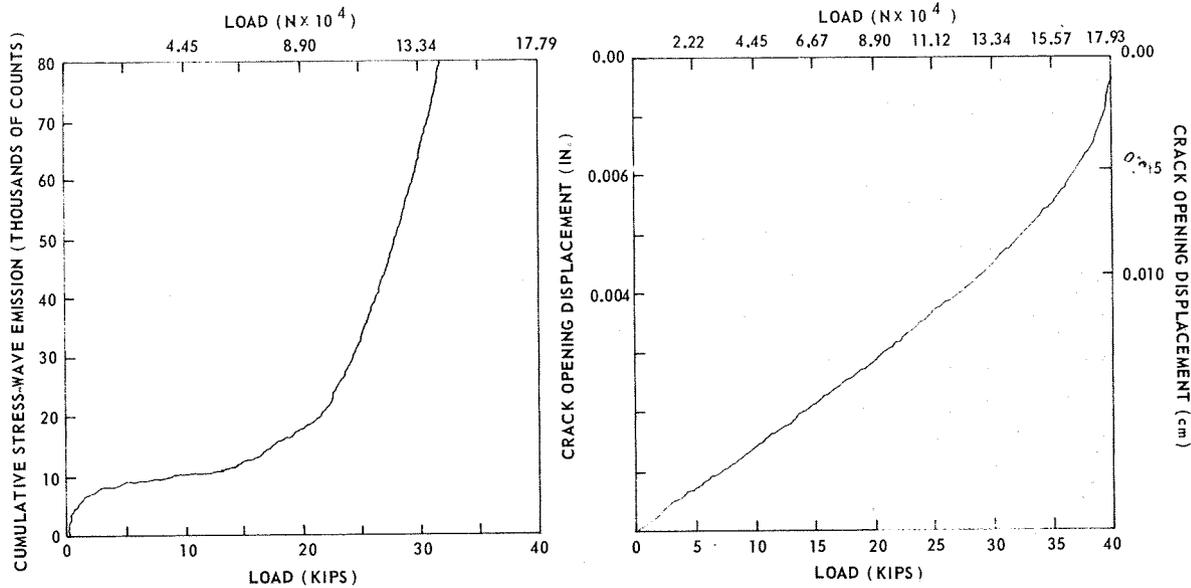


Figure 5. Test data for 7075-T73 aluminum PTC specimen tested at room temperature.

illustrated in Figure 6. Obviously, the increased rate and total emission from flawed material gives adequate time for corrective action to avoid failure.

AN ULTRASONIC TECHNIQUE FOR MEASURING STRESS

Considerable effort has been devoted to the improvement of ultrasonic techniques of measuring stress. Basically, stress measurement with sound becomes a matter of measuring ultrasonic velocity with great accuracy. One method of accomplishing this is illustrated in Figures 7 and 8. Figure 7 shows part of a four-point loading system used to place the top surface of a bar in tension. Ultrasonic energy is transmitted into the bar at point "A" and received at point "B". Transit time of ultrasonic waves in the bar is proportional to stress. Basically, many factors affect the time required for sound to travel the distance between the two ultrasonic transducers. However, all of these factors except stress remain constant for a particular material. Subsequent to adequate calibration, ultrasonic velocity changes from a base value for a specified material can be related to stress.

An electronic technique of tuning ultrasonic frequency until a specified number of wavelengths exist between the two transducers is used in the instrumentation system shown in Figure 8. Thus, frequency changes become a measure of ultrasonic

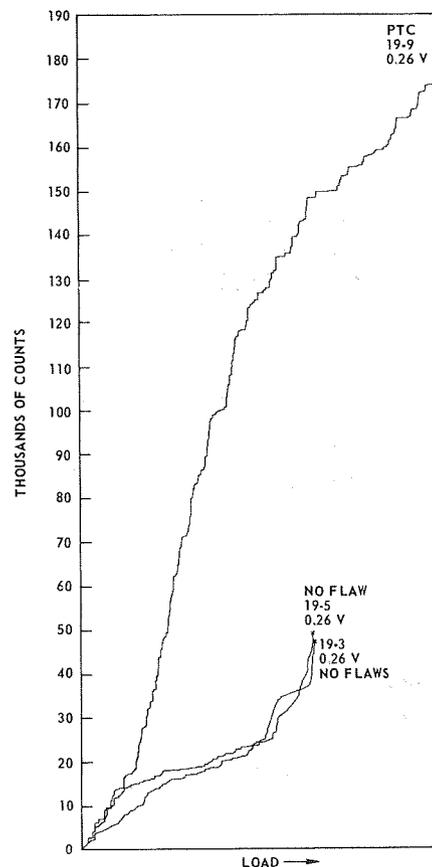


Figure 6. Effect of surface flaw on stress wave emission count; 2219-T87 parent metal tested at 77.59°K (-320° F).

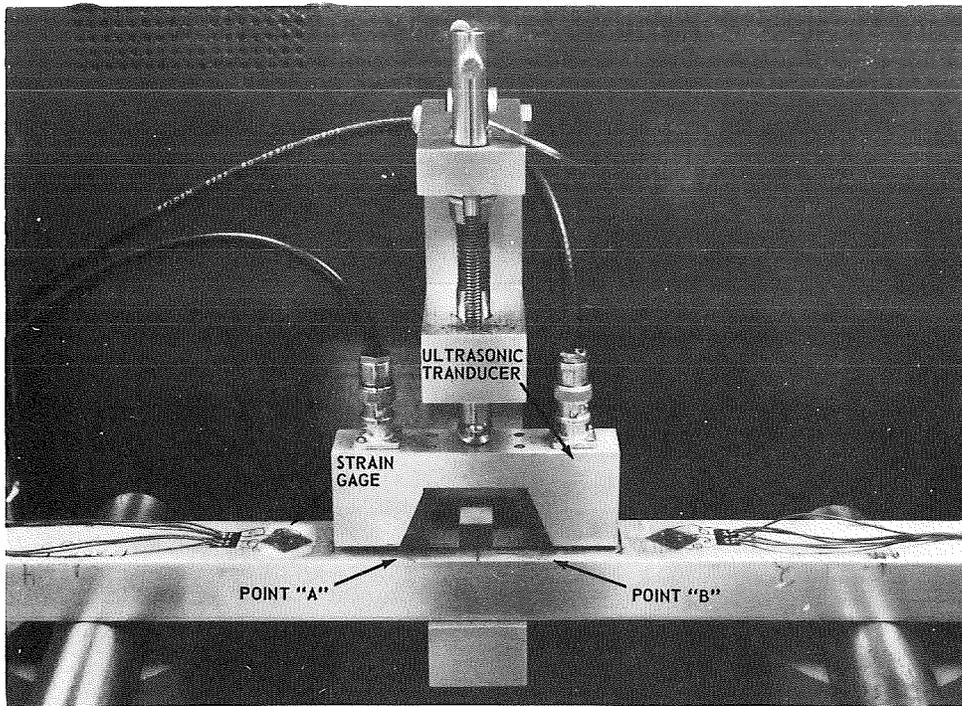


Figure 7. An ultrasonic system for measuring stress.

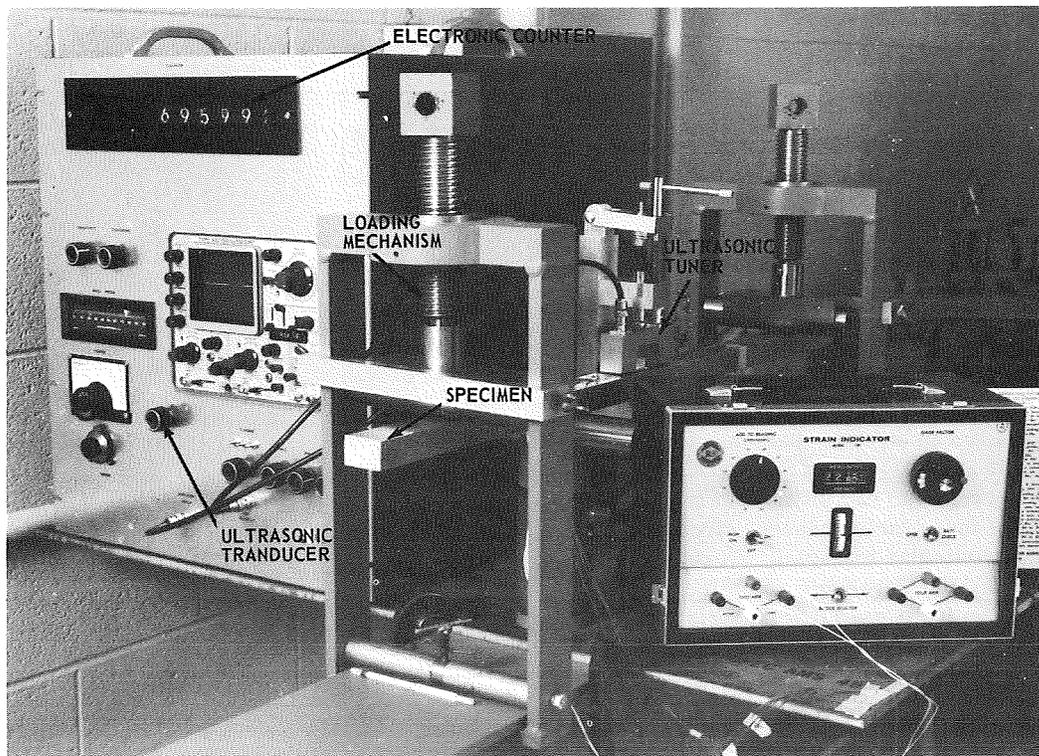


Figure 8. Ultrasonic transducer and clamp attached to a stressed bar specimen.

velocity changes and, consequently, a measure of stress. Typical results of ultrasonic stress measurements are presented in Table 1.

SUMMARY AND CONCLUSIONS

Significant progress has been made in developing nondestructive methods of evaluating the integrity of structural materials. Methods of special interest, developed or sponsored by MSFC, include

specialized techniques of debond detection, fatigue and stress corrosion "damage" measurement, monitoring crack growth, and ultrasonic stress measurement. These and more conventional NDT methods can be adapted for use in automatic monitoring systems for the Shuttle and Space Station. Although basic NDT technology is adequate for building automatic inspection systems, extensive work is required in selecting structural components to be monitored and in the development of flight hardware. Furthermore, the establishment of adequate inspections and standards represents a major effort.

TABLE 1. TYPICAL RESULTS OF ULTRASONIC STRESS MEASUREMENTS

Load on Bar N (lb)	Stress (Strain Gage) $N/m^2 \times 10^6$ (psi)	Stress (Ultrasonic) $N/m^2 \times 10^6$ (psi)
14 825.9 (3 333)	21.86 (3 170)	15.93 (2 310)
29 651.8 (6 666)	43.16 (6 260)	37.51 (5 440)
44 482.2 (10 000)	64.39 (9 340)	64.12 (9 300)
59 308.1 (13 333)	85.70 (12 430)	84.81 (12 300)
74 134.1 (16 666)	107.70 (15 620)	104.73 (15 190)
88 964.4 (20 000)	129.69 (18 810)	119.76 (17 370)
103 790.4 (23 333)	150.24 (21 790)	151.20 (21 930)
118 616.3 (26 666)	169.50 (24 700)	177.26 (25 710)
133 446.7 (30 000)	193.19 (28 020)	200.02 (29 010)
148 272.6 (33 333)	215.53 (31 260)	223.46 (32 410)

NUCLEAR MATERIALS TECHNOLOGY DEVELOPMENT FOR SPACE STATION AND NUCLEAR SHUTTLE

By

R. L. Gause

INTRODUCTION

The role of nuclear power in the exploration of space will take a giant leap forward in the late 1970's with the development of the Space Station and the Nuclear Shuttle. Studies [1] have shown that a nuclear reactor power system is extremely attractive for the generation of the electrical energy required to power a large, long lifetime, space station. Also, it appears that a nuclear-propelled vehicle is the most economical system to fulfill the requirements for a low cost reusable space transportation system to support long-term, high energy missions such as synchronous orbit and lunar surface bases or manned planetary excursions.

Regardless of whether it is to generate electrical power or to provide propulsive energy, the utilization of nuclear reactor systems for space vehicles impacts the design of these vehicles. This impact results from the radiation environment associated with the operation of a nuclear reactor. How nuclear radiation affects materials and systems integrity and performance is of vital importance and must be known in order to design a vehicle that will function reliably for the duration of its intended mission. Thus, sufficient data must be available to the designer to permit him to select materials whose properties will not be degraded by this environment. Of course, the specific data that are needed depend on the material, its function, the radiation type and intensity, length of exposure, and other factors. The purpose of this paper is to present this information for the Space Station and Nuclear Shuttle by qualitatively analyzing the indigenous radiation environment associated with each vehicle and assessing the effects of this environment on the types of materials required for its construction. In addition, the technology effort being pursued to develop the nec-

cessary radiation effects data is described, and typical experimental results are presented.

SPACE STATION ANALYSIS

System Description

One of the proposed orbital configurations for a Space Station utilizing a nuclear power generator is shown in Figures 1 and 2 [2]. The Nuclear Power System (NPS) is extended out from one end of the Space Station to maximize the separation distance between the reactor and the station and to minimize the angle subtended by the station. This is done to decrease the radiation dose to the manned portion of the Space Station. During nuclear operation, the NPS is moved out of the thermal structural shroud via the deployment system shown in Figure 3. Deployment is accomplished by means of a motor-drum-cable system that moves the NPS on rollers that engage rails in the elevator and radiator.

The power system consists of a zirconium-hydride (ZrH) compact reactor heat source and a lead telluride (PbTe) thermoelectric (TE) converter power-conversion system designed to produce 25 kW of electrical power (kWe). The system operates by means of two fluid transfer loops, the primary loop that transports heat from the reactor to the hot side of the TE converter and a heat rejection loop that transports waste heat from the cold side of the TE converter to the radiator. Both heat transport loops incorporate NaK-78 (a eutectic mixture of sodium and potassium) as the heat-transfer fluid. The design lifetime of the system is 2 years minimum with a goal of 5 years. End-of-life (EOL) disposal is to be accomplished using solid rocket motors to provide either (a) controlled deboost into deep ocean areas or (b) boost into a 400- to 500-mile orbit

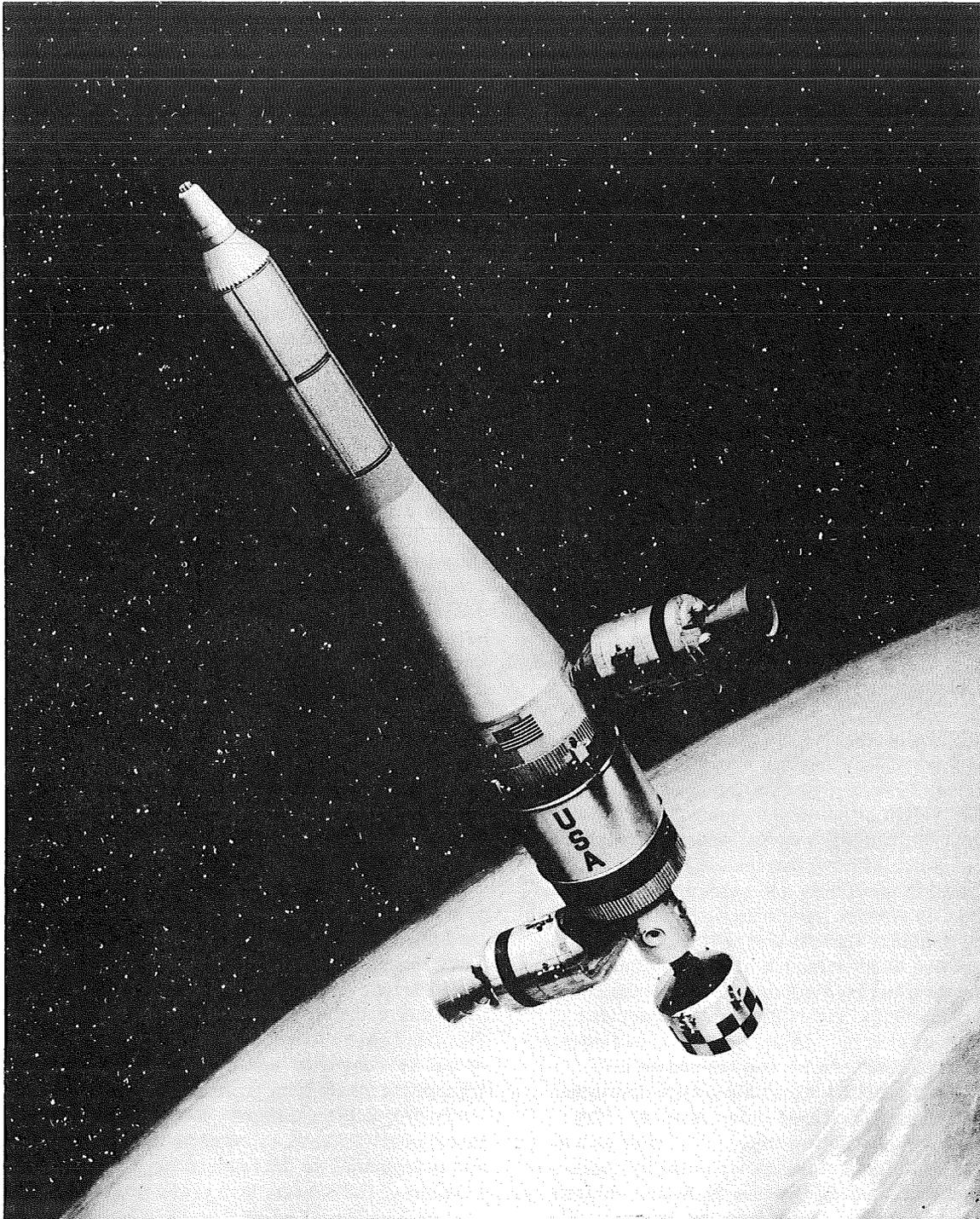


Figure 1. Space Station with Nuclear Power System.

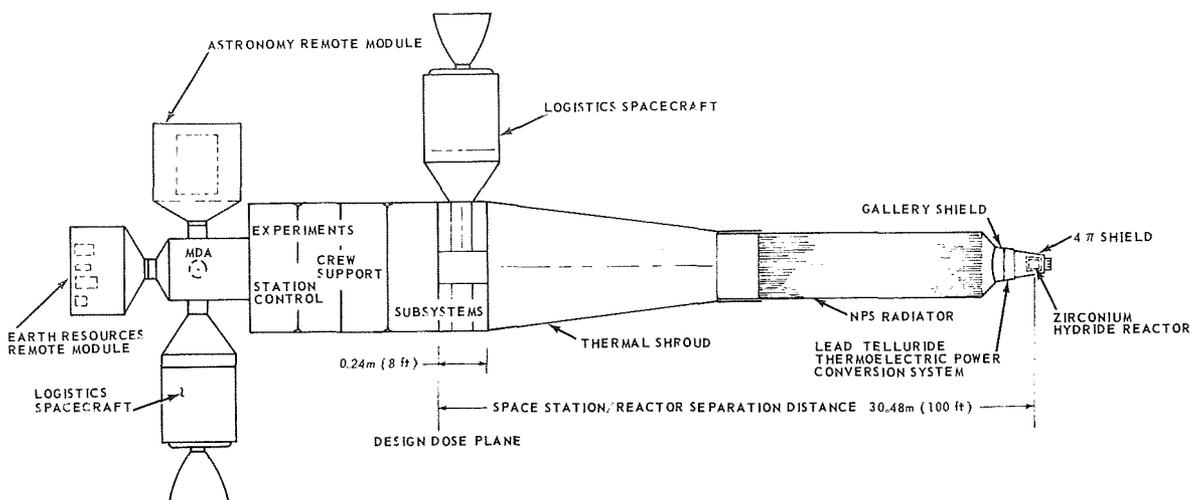


Figure 2. Space Station/Nuclear Power System configuration.

where the orbital decay time is sufficient to allow the fission-product activity to fall to a safe level.

Radiation Effects Considerations

The radiation environment will consist of the neutron and gamma radiation fluxes produced by the 600 kW thermal (kWt) reactor. Because of the neutron and gamma shields provided in the vicinity of the reactor, materials in the NPS outside the reactor will be exposed to low radiation fluxes. However, because of the long operating life of the system, the fluence (total integrated flux) will be high. Thus, materials such as thermal insulations, electrical insulations, potting compounds, and thermoelectric materials used in the construction of the thermoelectric modules will be subjected to a low flux, high fluence environment. Because the properties of these materials are critical to the efficient performance of the NPS, even small radiation-induced changes in thermal or electrical conductivity, or thermoelectric efficiency could have a significant effect on system operation.

As mentioned previously, the NPS is deployed on rollers by a motor-drum mechanism. Obviously, lubricants will be required for the rollers as well as in the motor bearings. Of course, only lubricants whose properties are not affected by long duration exposure to radiation and vacuum should be selected for these applications.

The major safety problem associated with the use of a nuclear reactor power system for the Space Station is the satisfactory disposal of the reactor after sustained operation in orbit. It was previously mentioned that the EOL disposal would be accomplished using solid rocket motors. These rocket motors will be located at a distance from the reactor such that the fluxes will be very low and the total exposure will be on the order of 10 to 10^2 J/kg (10^3 to 10^4 rads). Generally, this is considered to be a relatively low dose. However, even fluxes as low as this can produce large quantities of gases in some materials. In the case of the solid rocket, the gases cannot easily escape, and thermal cycling of the motor could result in cracks in the propellant because of stresses produced by the expansion and contraction of the radiation-induced gases. If such cracks occurred, they could seriously affect the performance of the rocket and jeopardize the safe disposal of the reactor.

The above brief analysis of some of the potential effects the radiation environment produced by the NPS could have on materials and systems performance is summarized in Table 1. The analysis was, of course, not intended to be comprehensive, but was made to indicate the type of evaluation that is required to determine if a vehicle is adequately designed from a radiation effects standpoint.

REACTOR - THERMOELECTRIC SYSTEM

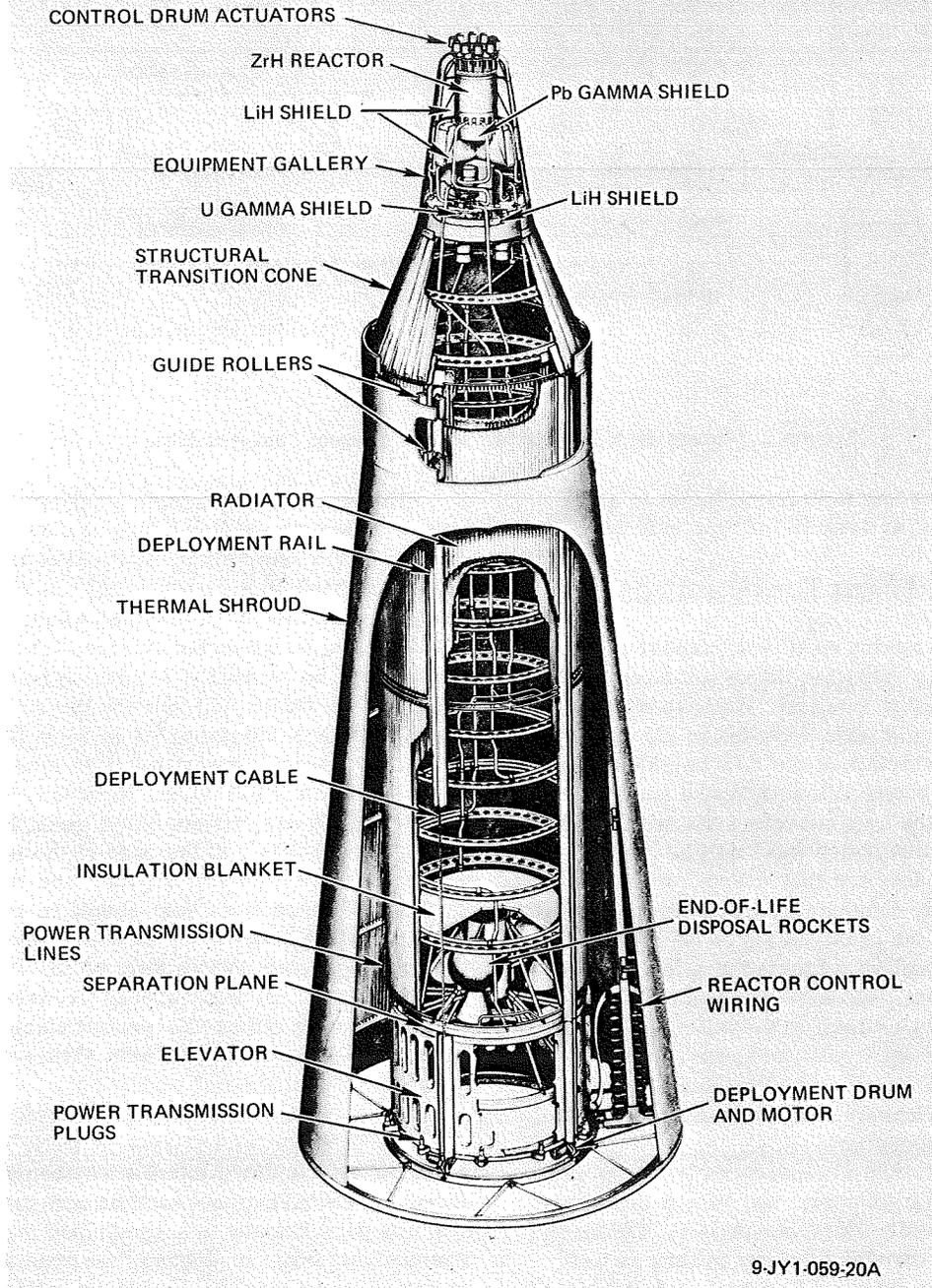


Figure 3. Nuclear Power System.

TABLE 1. SPACE STATION RADIATION EFFECTS CONSIDERATIONS

● Space Station Nuclear Power System (25 kWe, 600 kWt)
Radiation Environment:
Low Flux Level
Long Exposure Time (Years)
High Fluence
Space Environment:
Vacuum
Thermal
Synergistic Effects:
Thermoelectric Materials
Lubricants
Thermal Insulations
Electrical Insulations
Potting Compounds
Solid Propellants

NUCLEAR SHUTTLE ANALYSIS

System Description

The Nuclear Shuttle (Fig. 4) will be designed for a wide range of applications, multiple reuse, and a lifetime of 2 years. It will be able to operate in either a manned or unmanned mode and will possess the capability of long-term storage in space of its liquid hydrogen propellant. In addition, it will have the ability to station-keep in orbit between missions and to be refueled either by in-orbit transfer of propellant or by replacement of its propellant tanks.

The Nuclear Shuttle will be powered by the NERVA I nuclear engine, which will have a design operating lifetime of 10 hours. Inherent with the operation of this engine will be a high intensity

neutron and gamma radiation environment. Even with shielding, the radiation fluxes in the aft-bulkhead region of the vehicle will be high. Thus, in contrast to the NPS, where the flux levels were low and the exposure time was long, the Nuclear Shuttle flux levels will be high and the exposure time short. However, in both cases, the fluence will be relatively high.

To satisfy the long life requirement for the Shuttle, a high performance insulation system and special low leakage valves will be necessary for the conservation of propellant. In addition, a protective structure will be provided to prevent penetration of the propellant tank by meteoroids.

Radiation Effects Considerations

The materials that will be located in the aft-bulkhead region of the Nuclear Shuttle will be exposed to the highest radiation fluxes and are the ones that must be most radiation resistant. Typical materials that will be used in this region (excluding metals that have high radiation resistance) include thermal and electrical insulations, structural adhesives, valve seals, lubricants, and potting compounds. In addition to the radiation environment, these materials will also be subjected to vacuum and thermal cycling. This combined radiation-vacuum-thermal environment can drastically change the properties of many of these materials. Thus, the selection of materials and the design of systems for this area are critical and should be based on data obtained from simulated environmental tests.

A special radiation effects problem (known as nuclear propellant heating) arises from the deposition of nuclear energy in the propellant during engine operation. This can affect the thermodynamic state of the propellant by inducing stratification, increasing tank pressure, etc. Further analytical and experimental studies of this effect are necessary before the propellant system for the Shuttle can be adequately designed.

A summary of the above discussion of the Nuclear Shuttle is given in Table 2.

MATERIALS TECHNOLOGY PROGRAM

Thus far, this paper has presented in capsule form an analysis of the potential radiation effects

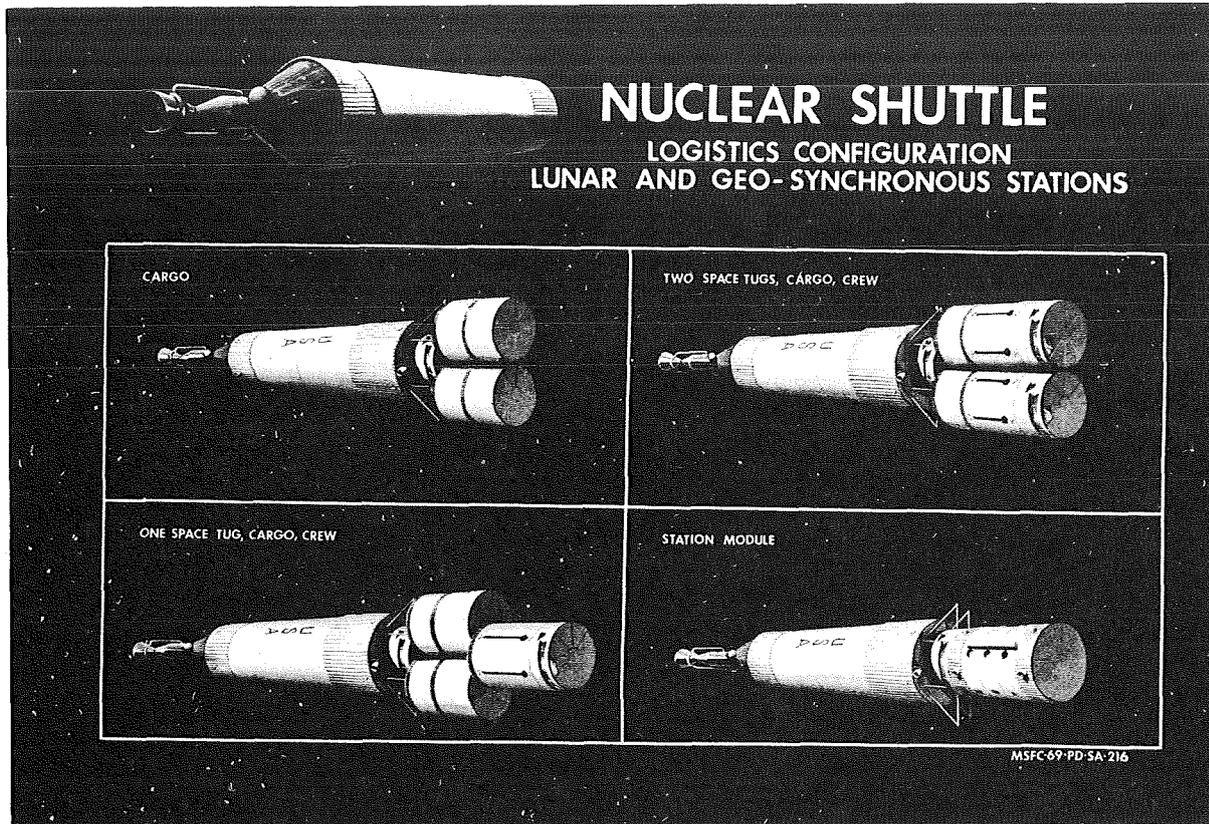


Figure 4. Nuclear Shuttle configurations.

TABLE 2. NUCLEAR SHUTTLE RADIATION EFFECTS CONSIDERATIONS

<p>Radiation Environment:</p> <ul style="list-style-type: none"> High Flux Levels Short Exposure Time (hours) High Fluence <p>Other Environments:</p> <ul style="list-style-type: none"> Vacuum Thermal <p>Synergistic Effects:</p> <ul style="list-style-type: none"> Thermal Insulations Electrical Insulations Structural Adhesives Valve Seals Lubricants <p>Propellant Heating</p>

problems associated with the development of the Space Station and the Nuclear Shuttle. A discussion will now be given of the technology program that was initiated by the Materials Division, Astronautics Laboratory of Marshall Space Flight Center in 1961 to generate the fundamental knowledge and experimental data required to solve the types of problems presented. Basically, the technology program involves (1) the development of new radiation-resistant materials, (2) the evaluation of basic materials for use in radiation-vacuum-thermal environments, (3) investigation of the effects of radiation on composite materials and components, (4) the study of radiation-induced outgassing, and (5) the analytical and experimental investigation of nuclear propellant heating phenomena. A brief description of each of these efforts is given below.

New Materials Development

Currently, research is underway to develop two essential radiation-resistant materials, a low

leakage cryogenic seal and a high temperature fluid lubricant for use in vacuum. Several new materials have been fabricated that appear promising for these applications. The successful development of these materials will be of great importance to the design of the Nuclear Shuttle.

Basic Materials Evaluation

This effort [3-7] was initiated in 1961 and involves the investigation of the effects of radiation, vacuum, and temperature on the properties of a wide variety of engineering materials. Over 350 different materials in the categories of (1) thermal insulations, (2) electrical insulations, (3) structural adhesives, (4) potting compounds, (5) vapor barriers, (6) thermal control coatings, (7) lubricants, (8) seals, and (9) structural laminates have been evaluated for functional performance in combined environments of nuclear radiation-vacuum, nuclear radiation-cryotemperature, and nuclear radiation-

vacuum-cryotemperature. Figure 5 shows the radiation-cryotemperature data obtained for a fluorocarbon seal (Kel-F-81) and illustrates the synergistic effects that can be obtained when a material is simultaneously subjected to two or more environmental factors.

Composite Materials and Component Studies

The purpose of this program [8] is to evaluate the effects of radiation on various composite materials such as complex multi-material thermal insulations. Also, the radiation degradation of the performance of materials as seals in valves or as sensing elements in transducers is being investigated.

The value of a test program such as this is vividly illustrated by comparing Figures 6 and 7. Figure 6 shows a liquid hydrogen dewar that was constructed to evaluate the effects of radiation and cryotemperature on the thermal and mechanical

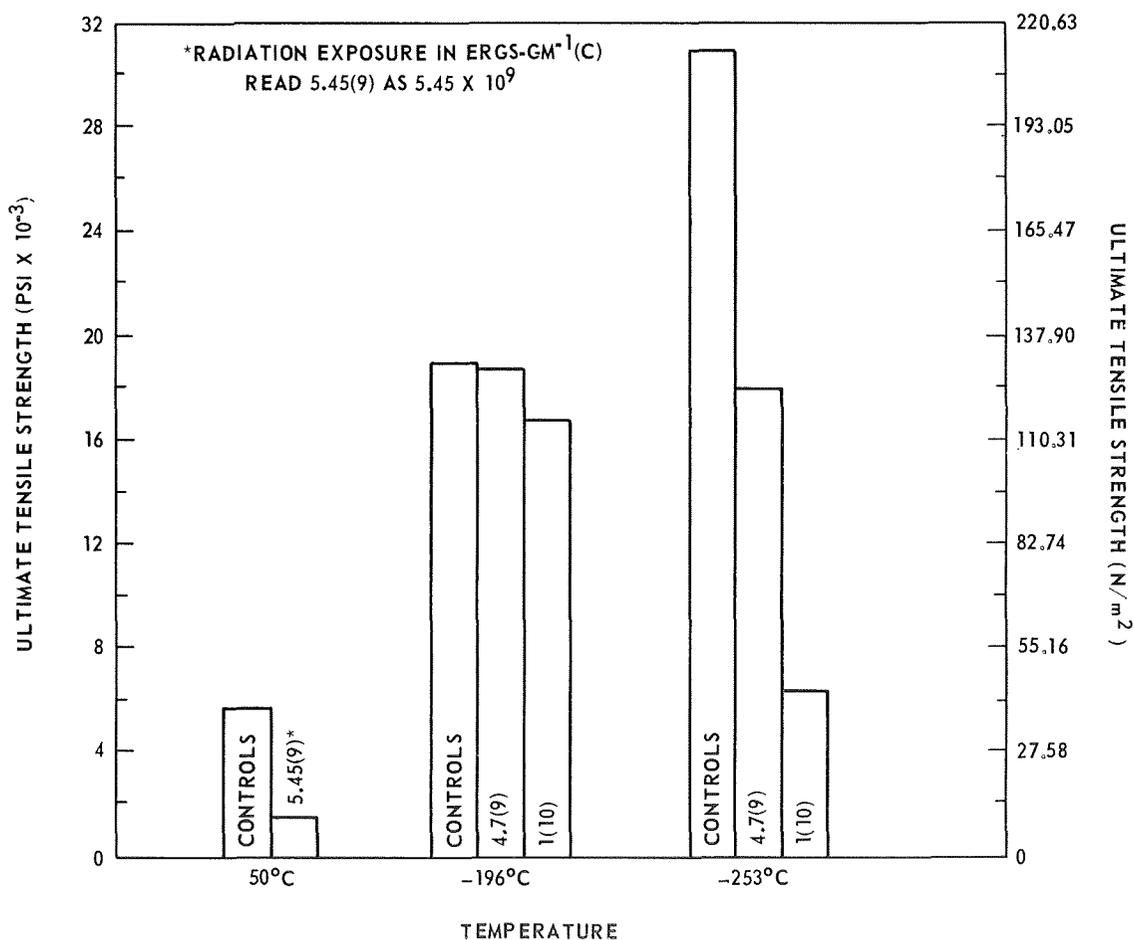


Figure 5. Radiation-cryogenic temperature data for a fluorocarbon seal (Kel-F-81).

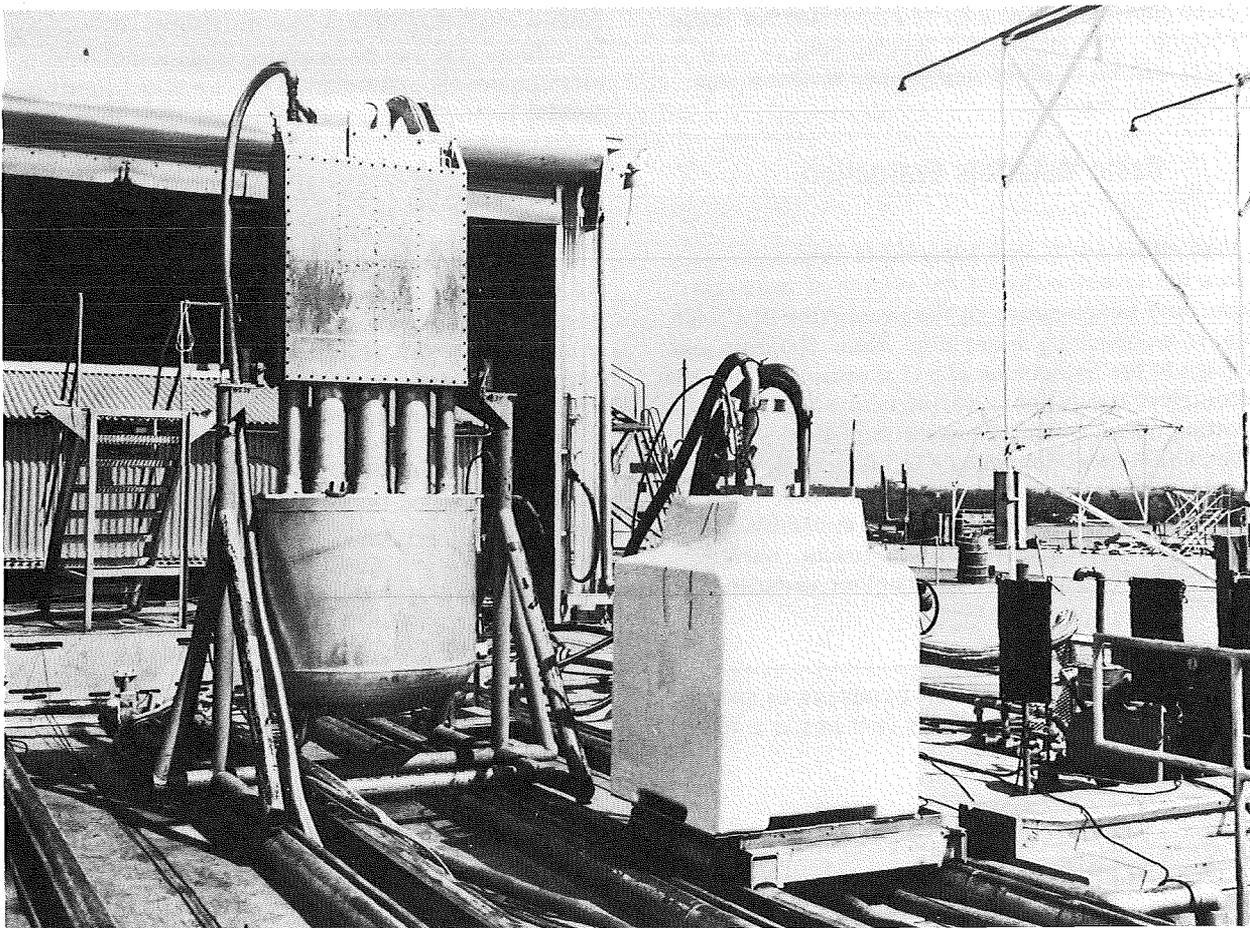


Figure 6. LH₂ dewar before irradiation.

performance of two thermal insulation systems. It was insulated on three sides with a polyurethane spray foam similar to the type used to insulate the S-II stage. The remainder of the dewar was insulated with corkboard. Both insulations were then covered with a resin impregnated fiberglass vapor barrier to prevent atmospheric gases and water vapor from entering the insulation and degrading its thermal conductivity. The dewar was filled with liquid hydrogen and irradiated to an approximate gamma dose of 1×10^{10} ergs-gm⁻¹(C). When this dose was achieved, detonations occurred in the corkboard insulation and produced the results displayed in Figure 7. Subsequent analysis showed that the detonations were the result of the reaction of radiation-induced hydrogen with air entrapped in the corkboard. The hydrogen was evolved by the corkboard as it was being irradiated. As the radiation exposure increased, the concentration of hydrogen increased, since the vapor barrier prevented the

hydrogen from escaping. The detonations occurred when the critical ratio of hydrogen to oxygen was reached. Obviously, it is of prime importance that results such as these are obtained in the laboratory and not on an operational vehicle.

Radiation-Induced Outgassing

As a result of the dewar test, a program was initiated to evaluate the radiation-induced outgassing characteristics of many of the plastic materials that have potential application on a nuclear vehicle such as the Nuclear Shuttle. The results obtained for ten common polymers are given in Table 3 in terms of G-values, where a G-value is the number of molecules of gas evolved for every 100 eV of energy absorbed by the material. This type of data will be of significant value in assessing potential gas evolution problems on the NPS and the Shuttle.

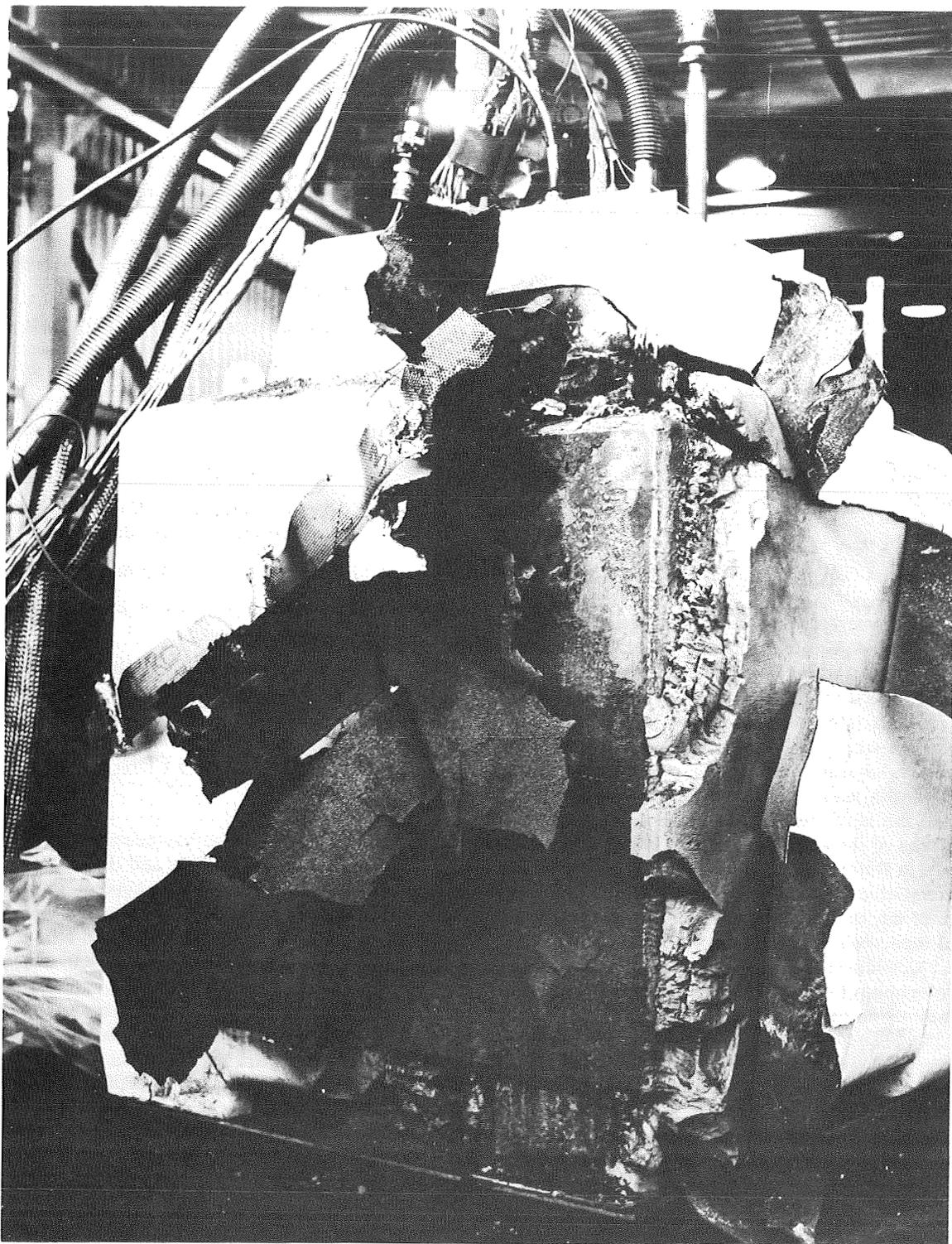


Figure 7. LH₂ dewar after irradiation.

TABLE 3. RADIATION INDUCED GAS YIELD (G) FROM SEVERAL POLYMERS

Polymer	G-Value ^a
Polyethylene	5.20
Polycarbonate (Lexan)	4.28
Cellulose Acetate Butyrate	4.28
Polypropylene	3.31
Polymethyl Methacrylate (Plexiglas)	2.01
Ethyl Cellulose	1.92
Phenolic (Bakelite)	1.72
Cellulose Acetate	0.64
Polyethylene Terephthalate (Mylar)	0.33
Polystyrene	0.26

a. G-Value — Number of Gas Molecules Evolved per 100 eV Absorbed

Nuclear Propellant Heating

The objectives of this program are (1) to obtain experimental data for evaluating existing calculational procedures designed to predict nuclear energy deposition rates and associated temperature distributions in liquid hydrogen and (2) to provide preliminary information with which to analyze vehicle systems response to changes in propellant tank configuration. The approach taken to accomplish these objectives involves the tasks outlined in Table 4. A detailed discussion of the analytical design of the experiment is given in Reference 8. However, since this effort was completed, significant changes that impact the design of the experiment have occurred in nuclear engine size, vehicle configuration, and operational mode. Consequently, efforts are underway to modify the experiment to satisfy the new requirements produced by these changes.

The experimental setup that will be used to obtain the data for this program is shown in Figure 8. The reactor is the 10 MW Aerospace Systems Test Reactor (ASTR) located at General Dynamics Corporation's Fort Worth Division in Fort Worth, Texas. Currently, this reactor is shut down because of operational difficulties. However, by the time the experiment is redesigned as mentioned previously, these difficulties should be resolved.

TABLE 4. NUCLEAR PROPELLANT HEATING PROGRAM OUTLINE

● Design Experiment
Multi-Parameter Test Matrix
Model Tank
Pumping System
Pressurization System
Instrumentation
● Fabricate and Assemble Required Hardware
● Conduct Irradiations on LH ₂ Tank
Flow Rates
Flux Levels
Pressure
Pressurant
● Measure Nuclear Radiation Fluxes, Temperatures, Pressures, etc.
● Correlate Data with Analytical Predictions
● Determine Validity of Existing Analytical Techniques
● Formulate New Propellant Heating Code (If Necessary)

SUMMARY AND CONCLUSIONS

A brief description has been given of the Space Station and Nuclear Shuttle and the impact which the nuclear reactors that will be used on these spacecraft will have on systems design and materials selection. Some potential radiation effects problems were presented to indicate the care that must be exercised in the design of these vehicles if they are to operate reliably for long periods of time in the space environment. Following this information, the technology program that is being pursued to generate design-oriented radiation effects data was briefly discussed and some selected experimental results were given.

In conclusion, it can be stated that the radiation environments that will be associated with the operation of the Nuclear Power System on the Space Station or the nuclear engine on the Nuclear Shuttle

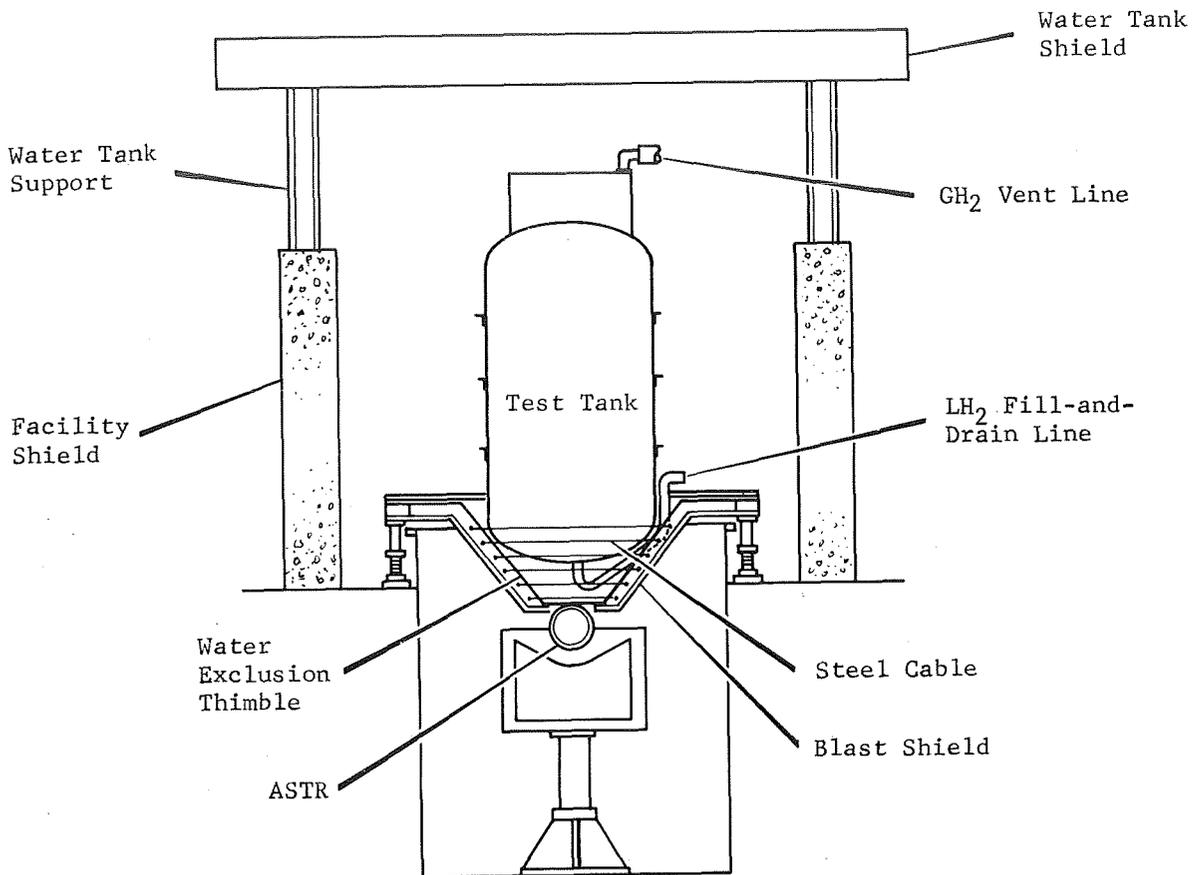


Figure 8. Schematic of propellant heating experiment test setup.

will not jeopardize the performance of these vehicles if the potential effects of these environments are considered in systems design, and vehicle materials are judiciously selected based on experimental radiation effects data.

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EXPLOSIVE BONDING POTENTIAL FOR SHUTTLE APPLICATIONS

By

O. Y. Reece

SUMMARY

High strength steel wire filaments and modular filament sheets were explosively bonded in metal matrices to form unidirectional filament reinforced composites. The lay-up procedures, explosives used, and problem areas are discussed, and the basic composite types are discussed with relation to potential Space Shuttle applications. Tensile data and photomicrographs of the explosively bonded interfaces are presented.

INTRODUCTION

Composites consisting of aluminum reinforced with high strength steel wire were first produced in 1964 by encapsulating alternate layers of steel wires and aluminum sheets in a vacuum retort and forge-pressing at high temperatures. Composites produced using this technique and having 25 percent unidirectional filament volume attained tensile strengths of 110.32×10^7 to 120.66×10^7 N/m² (160 000 to 175 000 psi) with a density of 99.8 kg/m³ (0.142 lb/in.³). These values are still comparable to those currently attained with some of the more exotic filament materials such as boron, silicon carbide, sapphire, and carbon. Therefore, it is believed that metal filament reinforced composites are currently competitive with other filament reinforced composites being considered for Space Shuttle applications.

Because of their elastic properties, high strength metal wire filaments can be forge-pressed into metal matrices without filament fracture, and they permit the matrix to sustain a higher percentage of the composite ultimate strength. Also, their elastic properties make metal filaments good candidates for explosively bonded wire-reinforced sheet composites.

Explosively bonded metal filament reinforced metal matrix composites should be considered for

Space Shuttle vehicle applications such as panel inserts, stringers, and possibly lower skin surfaces.

PROGRAM OBJECTIVES

The research conducted in this program was to prove and establish a relatively new technique for fabricating reinforced metal matrix composite sheets. The new process comprises the rolling of metal filament reinforcements into thin metal sheets and subsequently joining multiple sheet stacks by a single explosive joining operation. Several advantages of this explosive joining technique are apparent:

1. Excellent metallurgical bonds are obtainable.
2. No external heat is required.
3. A variety of metals can be bonded.
4. The process is inexpensive.

SCOPE OF WORK

The experimental work was completed in a three-phase study; i. e., explosive bonding of metal sheet laminates, explosive bonding of wire reinforced metal matrix composites, and explosive bonding of modular filament sheet reinforced metal matrix composites.

EXPLOSIVE BONDING OF METAL SHEET LAMINATES

Initial explosive bonding tests were conducted on aluminum alloy sheets for the purpose of establishing an acceptable explosive and determining layup procedures, buffer materials, and parting compounds.

Subsequent testing consisted of explosively bonding candidate matrix metals for filament reinforced composites and testing to determine possible dissimilar metal combinations that could be bonded.

Nitroguanidine explosive was selected for this experimental investigation because of its low detonation velocity (2438 to 3657 m/sec; 8000 to 12 000 ft/sec), low detonation sensitivity, cleanliness, and ease of establishing desired explosive densities. The explosive velocity of nitroguanidine is a function of its density as illustrated in Figure 1. Explosive load distributions and densities for successful bonding of aluminum alloy sheets ranged between 0.7 to 1.7 g/cm² and 0.28 to 0.4 g/cm³ respectively.

The lay-up or stacking sequence used for explosive bonding of metal sheet laminates is illustrated in Figure 2. This sequence consists of an absorber sheet (with paper adhesive tape bonded to both surfaces) positioned on a steel anvil. The matrix sheets with appropriate parallel stand-off between sheets are positioned above the absorber sheet. A buffer

sheet (with paper adhesive tape bonded to the lower surface) is positioned above the matrix sheets. Finally, the nitroguanidine explosive in a cardboard container is positioned above the buffer sheet. A blasting cap with tetryl booster attached is positioned centrally in one end of the explosive container. The paper tape, used as a stop-off to prevent the buffer and absorber sheets from bonding to the composite, was positioned with the slick face to the composite and was 0.02 cm (0.008 in.) in thickness. In most instances the buffer and absorber sheets were 0.318 cm (0.125 in.) thickness aluminum of any available temper. The buffer sheet and explosive should extend horizontally over the matrix sheets and absorber sheets by at least 3.81 cm (1.5 in.) on all four sides.

Utilizing this lay-up procedure and nitroguanidine explosive, a series of explosive bonding tests was completed on dissimilar combinations of 13 high purity metal sheets. Thirty dissimilar combination interface bonds shown in Figure 3 were successfully produced by the explosive technique.

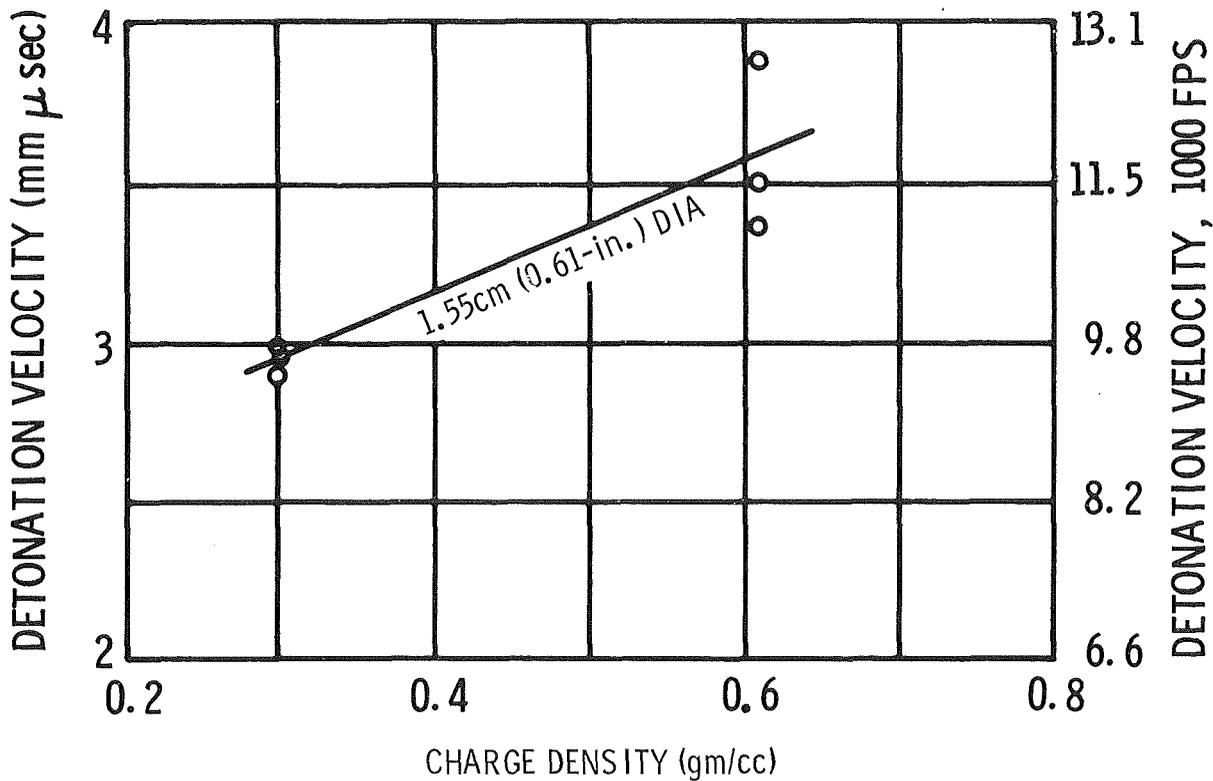


Figure 1. Explosive velocity of nitroguanidine as a function of its density.

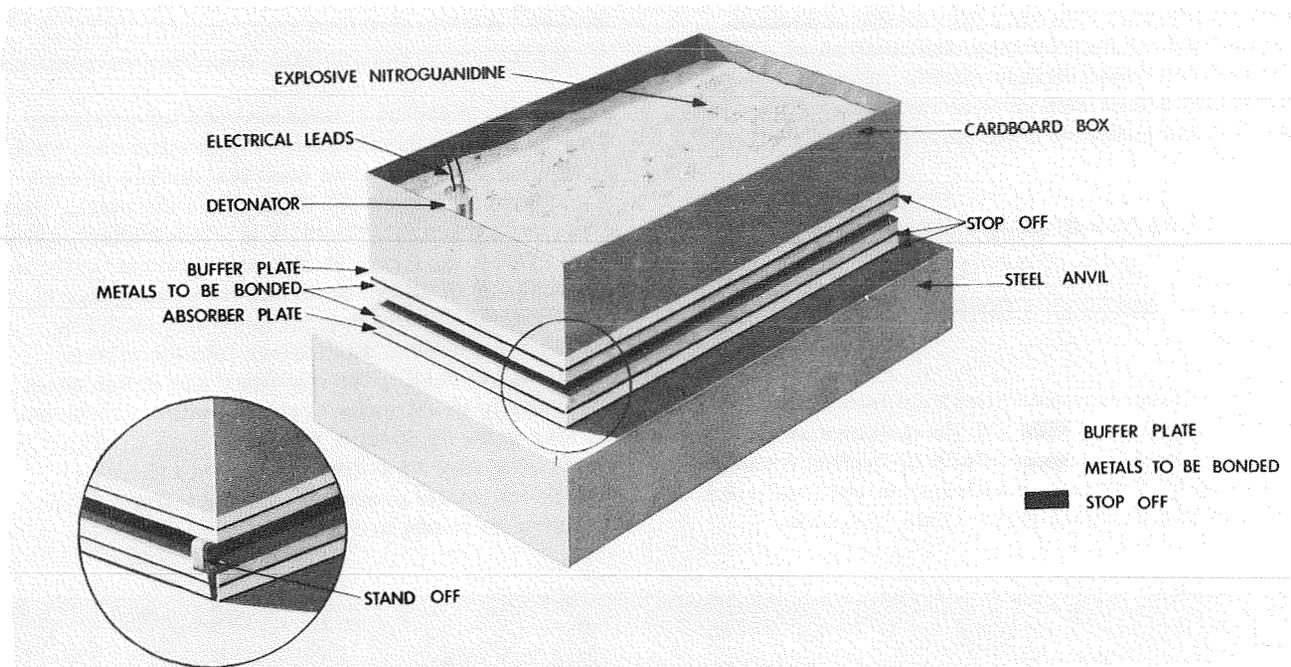


Figure 2. Typical explosive bonding lay-up.

	TITANIUM	VANADIUM	ZIRCONIUM	NIObIUM	TANTALUM	MOLYBDENUM	COPPER	IRON	STAINLESS STEEL
ALUMINUM	X	X	X	X	X	X	X		X
NICKEL	X	X	X	X	X				
COPPER	X	X	X	X	X	X		X	
IRON		X		X	X				
GOLD				X	X				
SILVER	X			X	X				
MAGNESIUM	X								X

Figure 3. Dissimilar metal combinations explosively bonded at Marshall Space Flight Center.

Potential Space Shuttle vehicle applications utilizing explosively bonded dissimilar metal laminates would include cladding of more reactive metals such as titanium with very thin sheets of passive metals such as high strength stainless steel. Other applications would include cladding of high strength refractory alloys with passive refractory alloys and possible formation of metal silicide sheet surfaces.

EXPLOSIVE BONDING OF WIRE REINFORCED METAL MATRIX COMPOSITES

Since forge-pressed aluminum matrix composites reinforced with AM 355 stainless steel wire had been produced successfully by Harvey Aluminum Company of Torrance, California in 1963 and 1964 under NASA Contract NAS8-11508, the same

matrix-filament combination was selected for providing the explosive bonding process. The aluminum alloys used were 1100-0, 2024-T4, 2014-T6, and 6061-0. AM 355 stainless steel wire in 0.0114 and 0.0229 cm (0.0045 and 0.009 in.) diameters were utilized.

The first lay-up procedure used for producing wire reinforced metal matrix composites consisted of winding wire filaments over the surface of each successive aluminum sheet placed in the stack. However, four types of defects, i. e., longitudinal splits, wavy filaments, filament fractures and non-uniform filament distribution, occurred when using this lay-up technique. These defects were eliminated by rolling the stainless steel wires into the matrix sheets and extending the explosive and buffer sheet horizontally or laterally over the matrix sheets on all four sides by about 3.81 cm (1.5 in.). The transverse view of a wire reinforced aluminum matrix composite produced with the latter lay-up technique is shown in Figure 4.

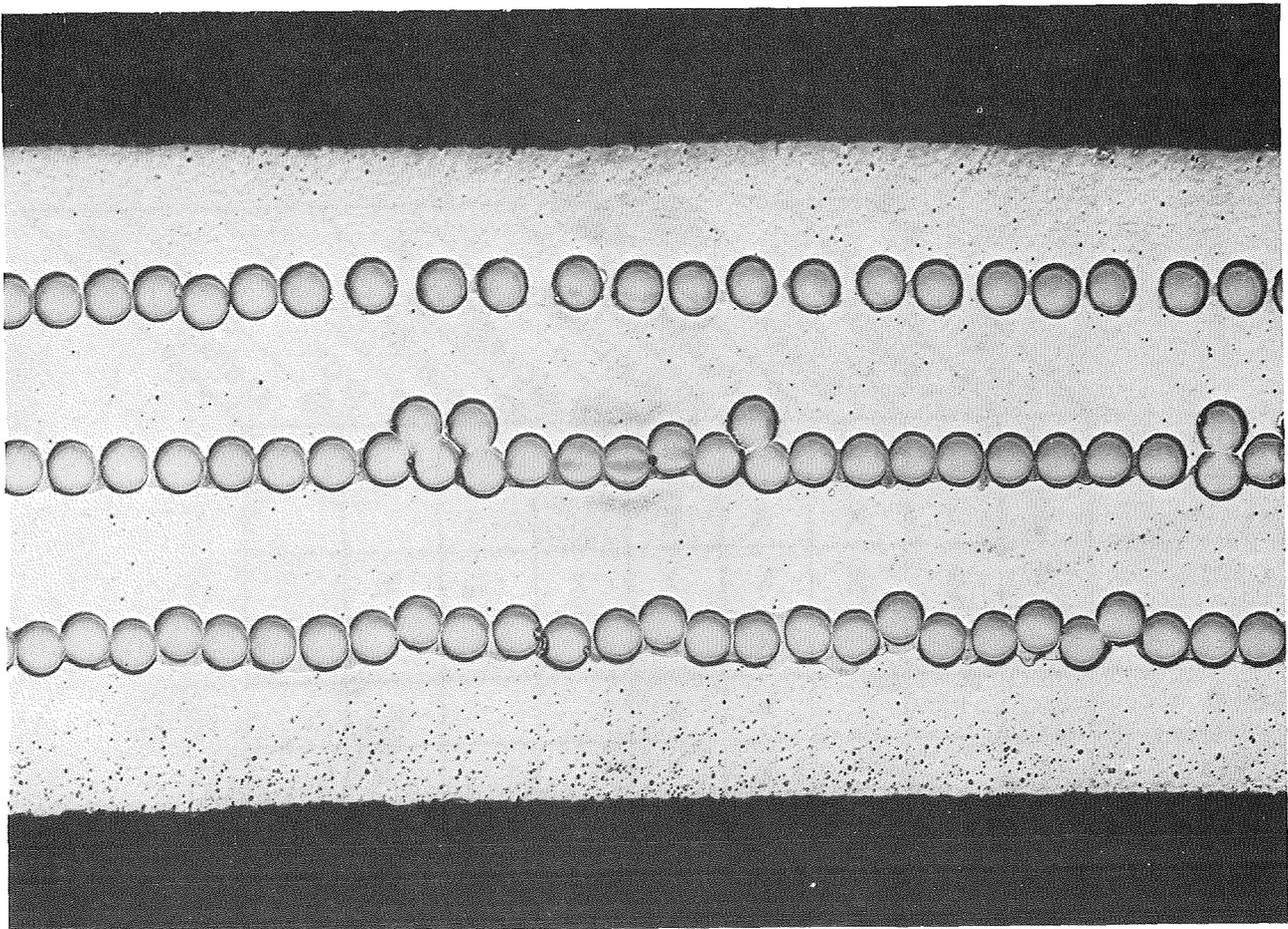


Figure 4. Photomicrograph of transverse view of an explosively bonded wire-reinforced composite.

Typical mechanical properties of a filament reinforced aluminum composite are presented in Figure 5. Tensile properties of the 1100-0 aluminum matrix sheets were approximately 89.63×10^6 N/m² (13 000 psi) before explosive bonding. Therefore, the 461.95×10^6 N/m² (67 000 psi) tensile strength of the explosive bonded composite is a significant improvement and exceeds calculated law-of-mixtures values. Tensile strength of the AM 355 stainless steel wires ranges between 275.79×10^7 and 344.74×10^7 N/m² (400 000 and 500 000 psi). Potential explosive bonded wire reinforced metal matrix composites utilizing 413.69×10^7 N/m² (600 000 psi) steel wire at 33 1/3 volume percent and 482.63×10^6 N/m² (70 000 psi) 2014-T6 aluminum matrix at 66 2/3 volume percent should exceed 170.09×10^7 N/m² (246 700 psi) tensile strength with a density of 4428.78 kg/m³ (0.160 lb/in.³). The strength-to-weight ratio of this composite would be

1 562 300 to 1. Space Shuttle applications utilizing wire reinforced metal matrix composites would include flat and curved skin surfaces; stringers; and, possibly, refractory alloy laminates reinforced with TZM filaments.

MODULAR FILAMENT SHEET REINFORCED METAL MATRIX COMPOSITES

Modular filament sheets are high strength metal sheets that have been machined or stamped in such a manner as to form rectangular filaments as shown in Figure 6. Filament sheets of the two patterns illustrated were fabricated from thin sheets of Custom 455 stainless steel, beryllium, and 6-4

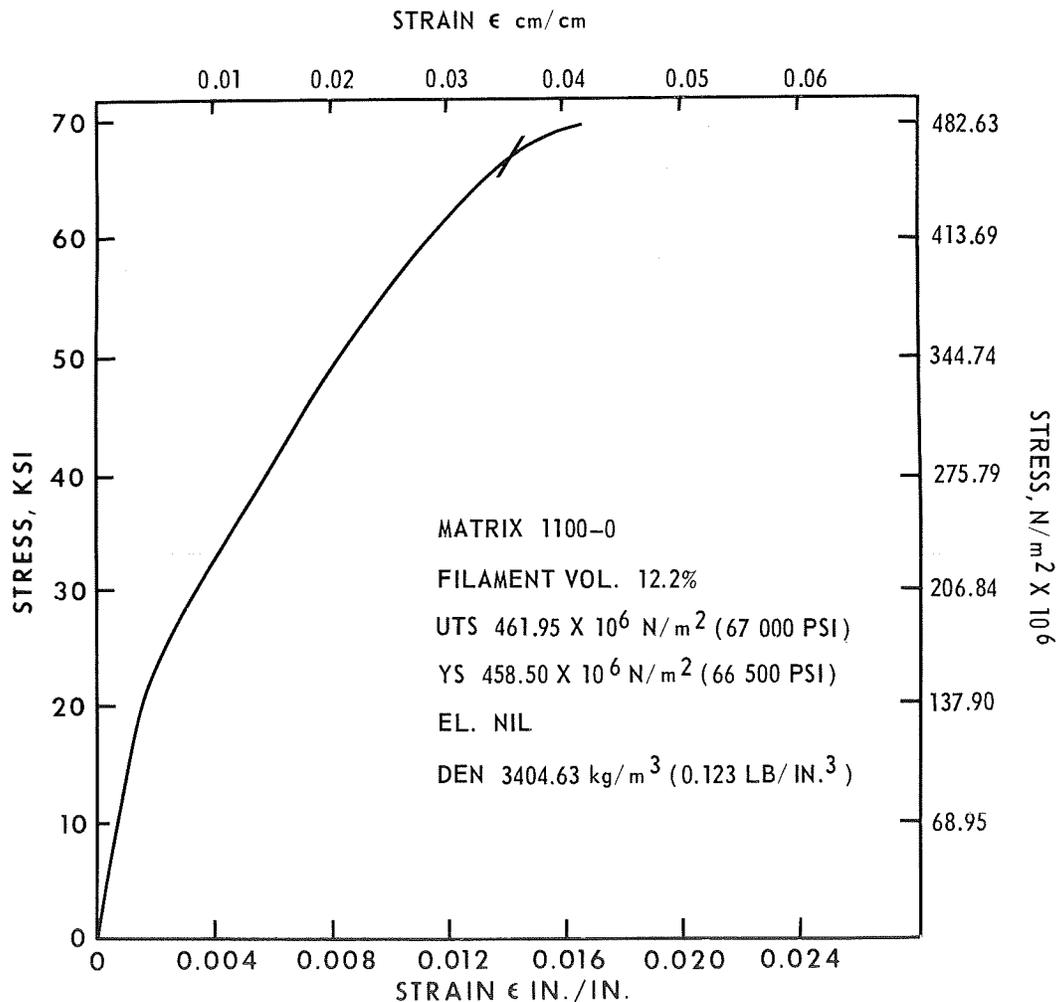


Figure 5. Stress-strain curve of an explosively bonded wire-reinforced metal composite.

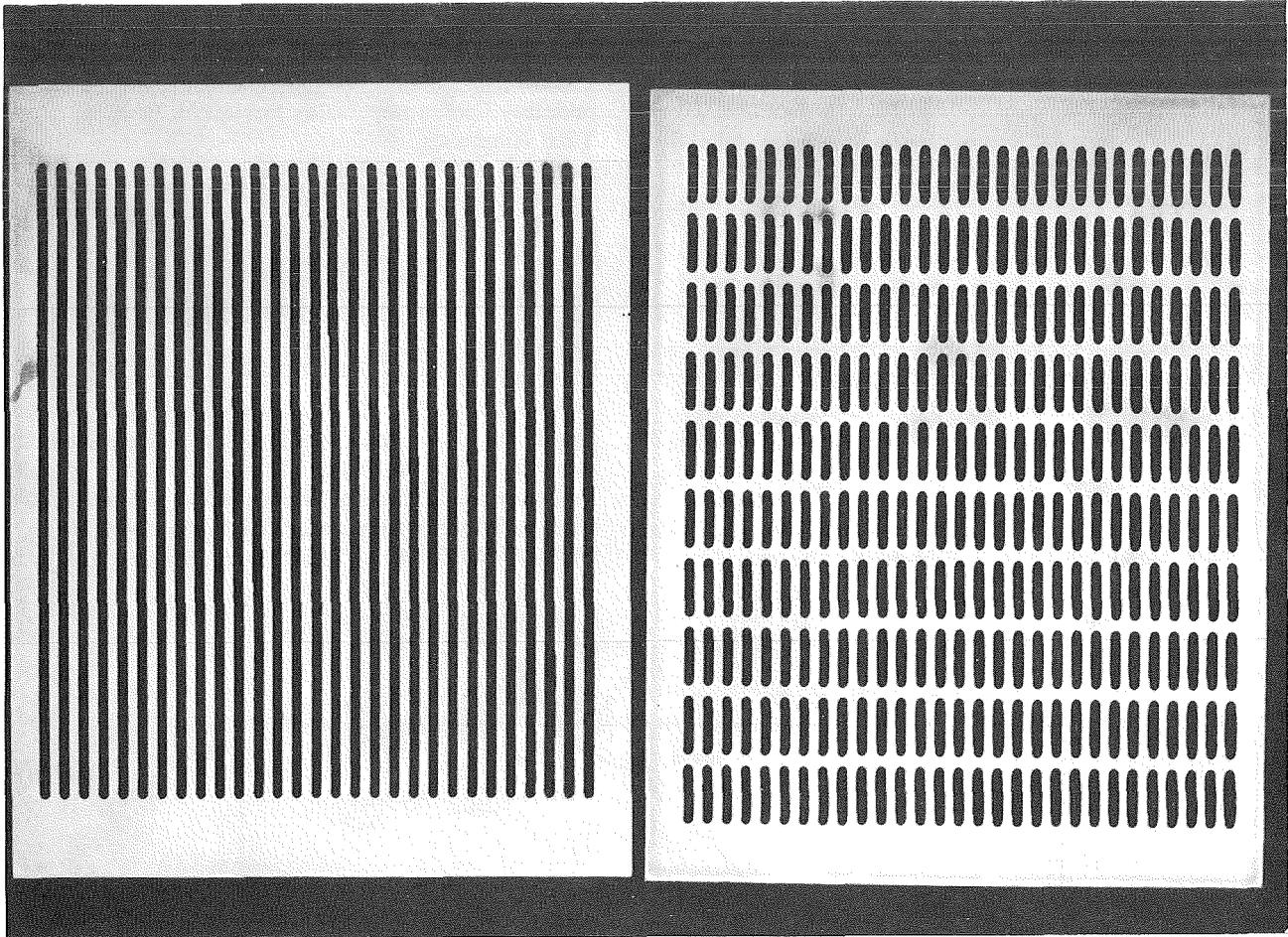


Figure 6. Illustration of two modular filament sheet patterns.

titanium alloy and explosively bonded in aluminum and magnesium matrices. Beryllium sheet proved unsatisfactory because of the brittleness of the alloy. Custom 455 stainless steel has a tensile strength of 179.26×10^7 to 193.05×10^7 N/m² (260 to 280 ksi) and proved to be a very good filament sheet alloy.

An explosively bonded 2014-T6 aluminum composite reinforced with Custom 455 stainless steel modular filament sheet as shown in Figure 7 was evaluated. The tensile properties attained in this composite were as follows: tensile strength was 649.49×10^6 N/m² (94 200 psi), yield strength was 620.53×10^6 N/m² (90 000 psi) and elongation was 3.5 percent. Stress-strain curves for the as-received

2014-T6 alloy and the explosively bonded composite are shown in Figure 8. The strength of this composite also exceeded the law-of-mixtures value.

CONCLUSIONS

Metal matrix composites have been successfully produced by explosive bonding, and they have a variety of potential applications in Space Shuttle vehicles. The lay-up configurations and explosive material are critical. Also, it is believed the process has been adequately proven to the extent that scale-up studies for production appear attractive.

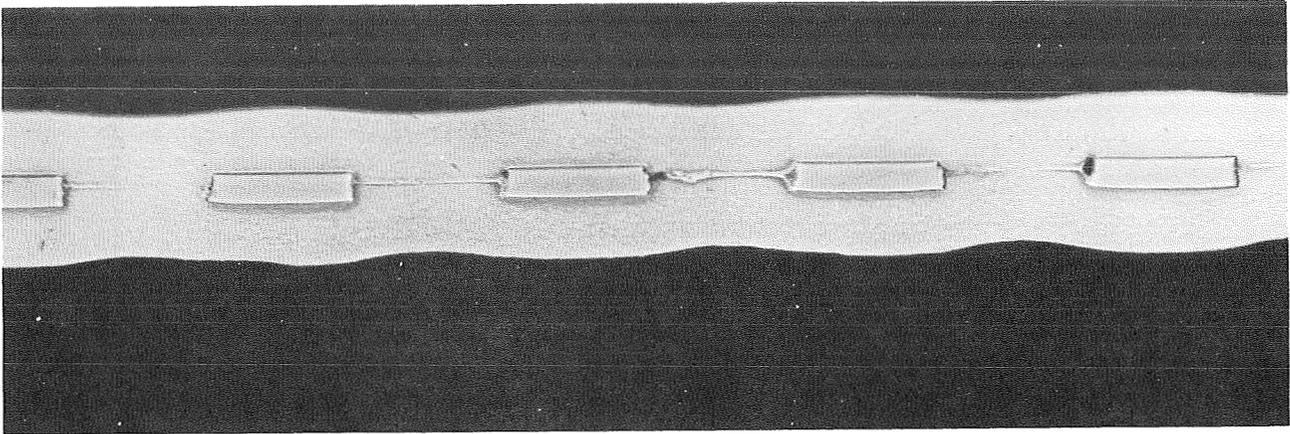


Figure 7. Photomicrograph of transverse view of an explosively bonded modular filament reinforced composite.

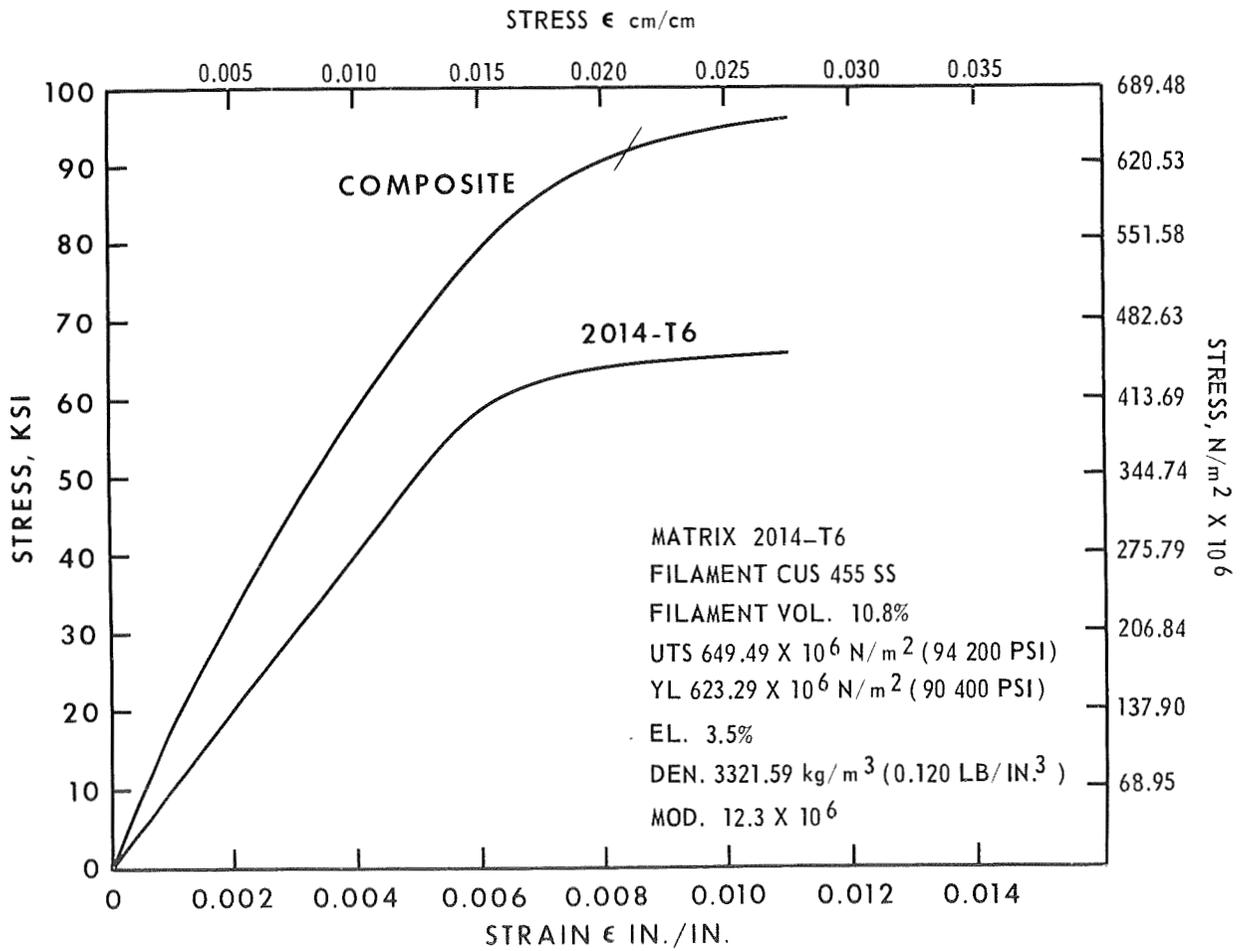
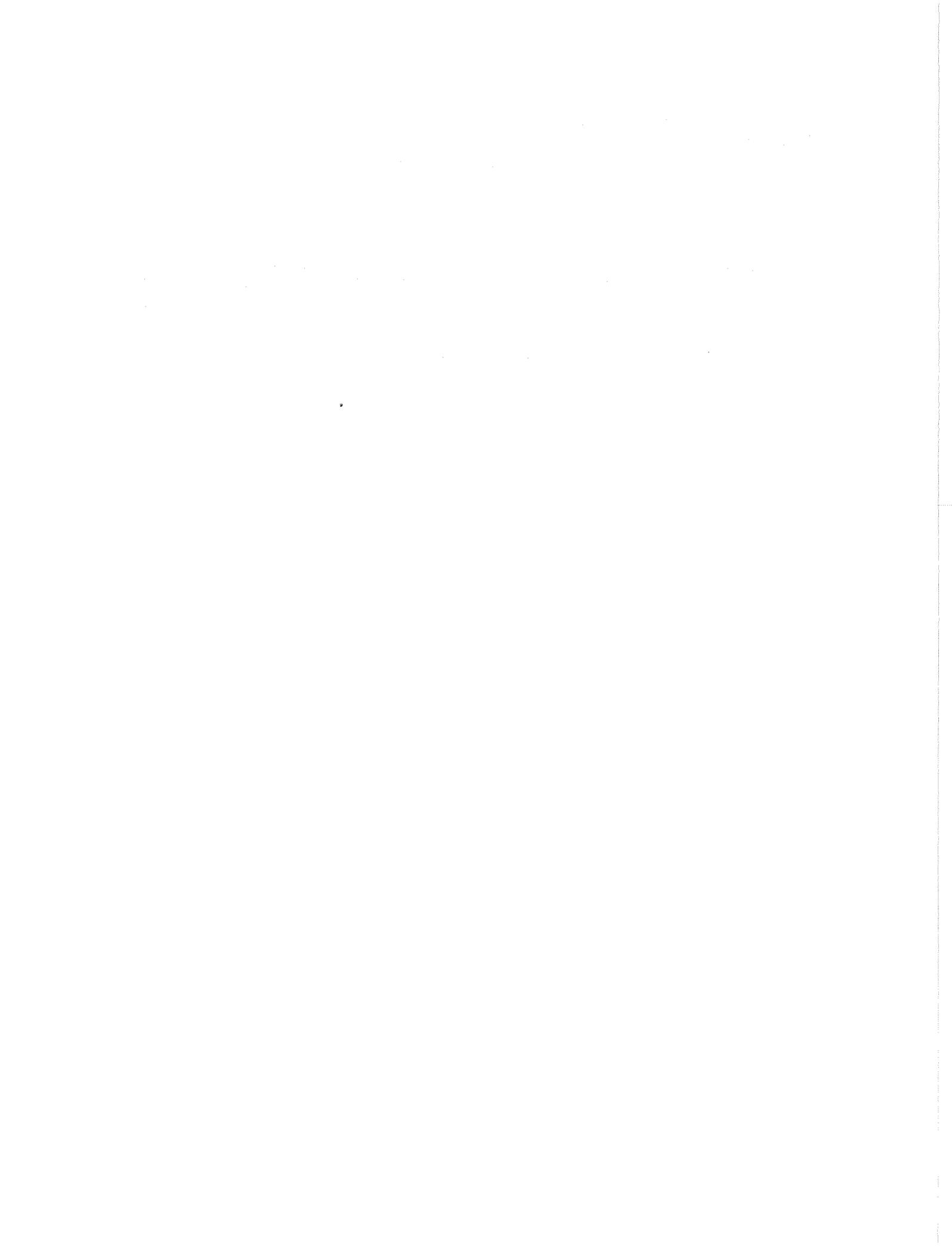


Figure 8. Stress-strain curve of an explosively bonded modular filament reinforced composite.



METAL MATRIX COMPOSITES FOR THE SPACE SHUTTLE

By

E. C. McKannan and F. P. LaIacona

INTRODUCTION

This paper discusses suggested metal matrix composite materials for the Space Shuttle in terms of (1) a cool primary structure and (2) the hot thermal shield. Boron-aluminum has been developed to the state of readiness for application in the Space Shuttle thrust structure. It has advantages of shear strength and joinability over other composite materials. Molybdenum wire reinforced nickel has advantages of high strength-to-weight ratio for standoff hardware in the thermal shield at high temperatures.

COOL PRIMARY STRUCTURAL MATERIALS

By far the largest quantity of material in the primary structure of the Space Shuttle will probably be aluminum alloy 2219 for very well known reasons; i. e., the accumulated experience that has been obtained with this alloy; its high strength; cryogenic properties; ease of fabricability, particularly weldability; and its stress corrosion resistance. However, for advanced high performance vehicles, a lightweight, high strength metal matrix composite has been suggested. This is essential in the thrust structure to make the vehicle less tail heavy and, therefore, to reduce nose ballast.

Boron-aluminum composite materials of 50 percent by weight aluminum alloy matrix can be made into large, thin sheets for the facing of honeycombs or for tubing and special cross sections for use in columns and struts. This material can be used at temperatures up to about 700°K (800° F), which is higher than the limit for parent aluminum alloys. It is currently available in sheets up to 0.37 m² (4 ft²) in area. This size is limited only by the currently available forge presses used in press-bonding the material.

Several successful applications of boron-aluminum have been reported. One of these is the interstage of the Atlas-Centaur vehicle in which the use of boron-aluminum replaced an aluminum-stiffened structure saving about 45 percent of the weight. Table 1 illustrates the nominal strength of this material at room temperature compared to the common aluminum alloy, showing the very high increase in strength and stiffness that is gained when boron-aluminum is used in the uniaxial stress condition parallel to the longitudinal direction of the filaments. When the material is used in applications requiring strength in several directions, fibers must be cross-wound, and the strength is somewhat reduced. Figure 1 is a strength-stiffness map that is a visual representation of the specific strength (i. e., the yield-strength-density ratio) plotted on one ordinate and the specific modulus (modulus-to-density ratio) plotted on the other ordinate of a log-log plot. The most desirable, stronger, and stiffer materials for a given weight would be to the upper right corner of such a plot. Conventional alloys are in the lower left corner, and the boron-aluminum shows its superiority in strength and stiffness to those materials. The point shown for boron-aluminum is (once again) the uniaxial case. When used in biaxial stress conditions, the fibers must be crossed, and the strength is somewhat reduced from this level.

Table 2 indicates some of the current problems with boron-aluminum composites. The boron filament is produced by vapor-depositing boron upon a 0.0025 cm (1 mil) diameter tungsten wire. The filament is wound and stretched between thin sheets of aluminum, and this composite is pressed into a structural shape. The interface between the boron filament and the aluminum matrix is of great interest. It was surprising to find that the interfacial strength comes from a mechanical bond in spite of the high re-activity of the boron. Oxides of aluminum are involved in the interface, and these tend to contaminate the bond. Sheets of this material are formed by several processes as listed in Table 2. The

TABLE 1. NOMINAL STRENGTH AT 296° K (75° F)

Property	Units	Al 2219	Be	B-Al
Density	kg/m ³ (lb/in. ³)	2823.35 (0.102)	1826.87 (0.066)	2584.23 (0.093)
Yield Strength	N/m ² × 10 ⁷ (ksi)	31.72 (46)	34.47 (50)	110.32 (160)
Modulus	N/m ² × 10 ⁹ (Msi)	75.84 (11)	303.37 (44)	227.53 (33)

most widely used is the hot press lamination for flat sheets. Liquid metal infiltration, however, is often used in tubing and shapes of small cross sections. Explosive bonding shows great potential for scaling up to large sheets.

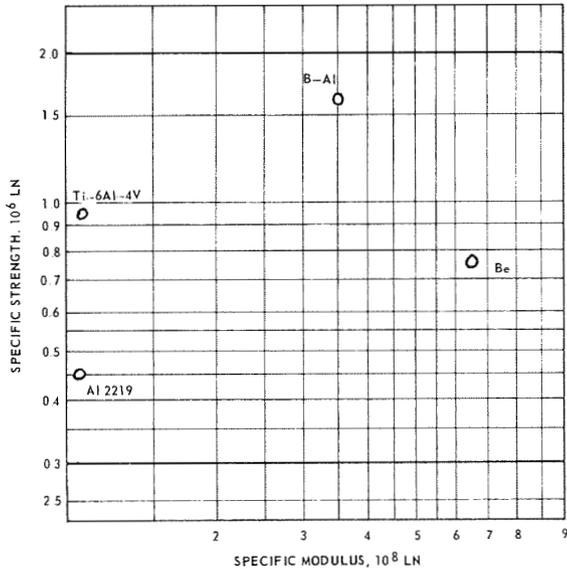


Figure 1. Strength and stiffness — density relationships for light alloys.

TABLE 2. BORON FIBER REINFORCED ALUMINUM

Fiber:	0.0102 cm (4 mil) Diameter
Interface:	Mechanical Bond Oxide Contamination Low Shear Strength
Forming:	Hot Press Lamination Liquid Metal Infiltration Explosive Bonding Plasma Spray Vapor Deposition Electrodeposition

Figure 2 is a microphotograph of a fracture surface taken from a test specimen and magnified 5000 times in the scanning electron microscope. The tungsten core of the filament and the rough surface of the deposit of boron are readily visible, showing that the boron surface has not been reacted or degraded in any way by either the processing or the breaking of the bond. The ductile shear fracture of the aluminum matrix is also obvious from the picture. It was necessary to improve the transverse and shear strength of the matrix, so other, stronger aluminum alloys were investigated, such as the precipitation strengthened alloy 6061-T4, which can be formed in the annealed condition and then heat-treated to the higher strength condition. Table 3 shows the strength of the annealed or soft condition of the composite as compared to the heat-treated or strengthened condition. It indicates that the heat treating did not degrade the boron or the boron-to-aluminum interface. The longitudinal strength and stiffness were not degraded. In the same material, the shear and transverse strengths through the matrix were improved.

Another area of great concern in the use of composite materials is that of joining. In many cases, doublers are required in the joint. The additional thickness and fasteners produce a reduction in the strength-to-weight ratio of the overall composite structure. Table 4 indicates that to use fasteners, holes must be drilled that break the filaments and the continuity of the material, and require additional material. Riveted joints often fail by shear through the composite material. Adhesive bonds are useful and are very strong in pure shear but are weak in peel strength and lack good thermal expansion characteristics, because the adhesive does not match the thermal properties of the metal matrix. Resistance

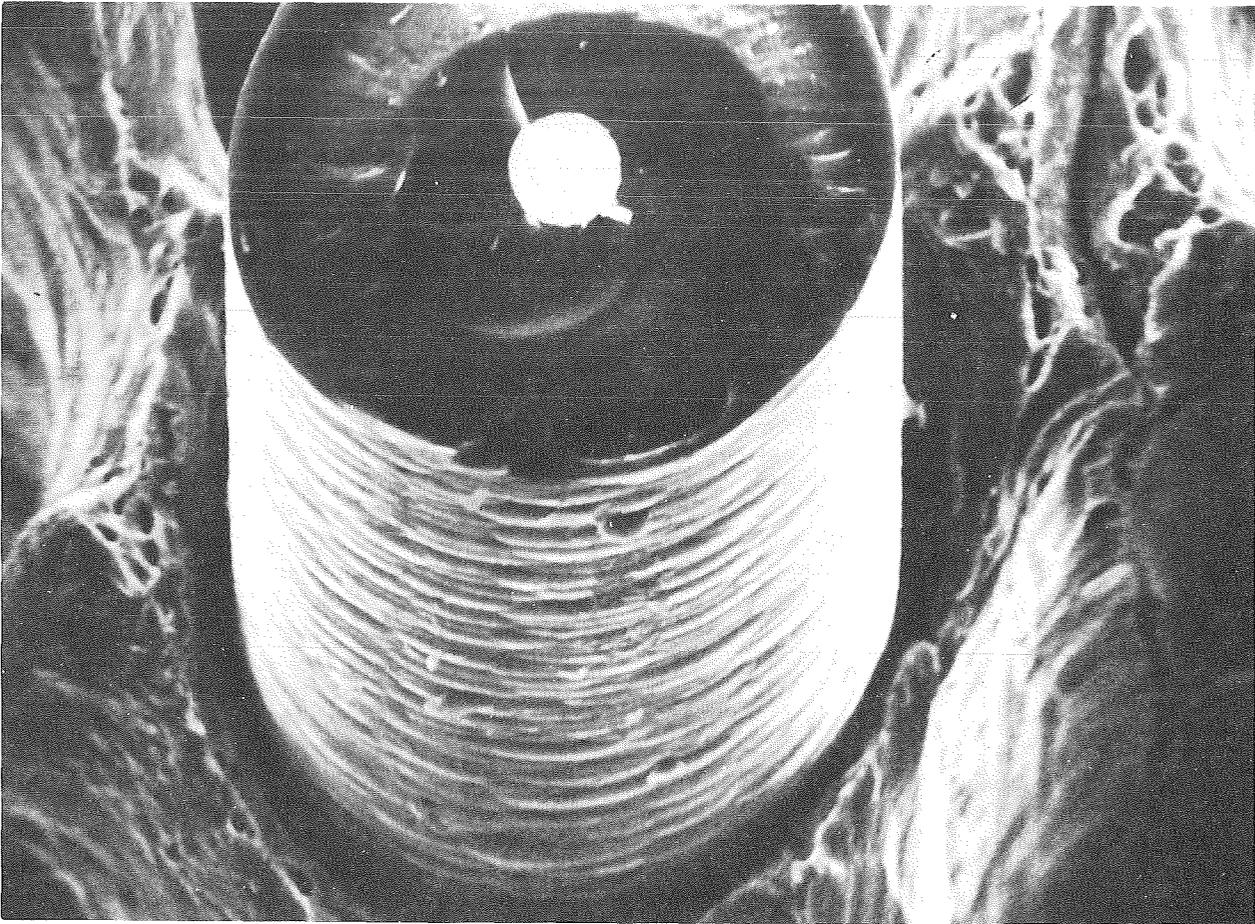


Figure 2. Microphotograph of boron-aluminum fracture surface at 5000X.

TABLE 3. THERMAL TREATMENT OF 50 PERCENT 6061 ALUMINUM-50 PERCENT BORON

Condition	Annealed	Solution Treated 800° K (980° F) Aging
Longitudinal Tensile Strength, $N/m^2 \times 10^7$ (ksi)	110.32 (160)	110.32 (160)
Longitudinal Modulus, $N/m^2 \times 10^6$ (ksi)	234.42 (34)	234.42 (34)
Transverse Tensile Strength, $N/m^2 \times 10^6$ (ksi)	96.53 (14)	151.68 (22)
Transverse Modulus, $N/m^2 \times 10^6$ (ksi)	151.68 (22)	151.68 (22)
Shear Stress, $N/m^2 \times 10^6$ (ksi)	89.63 (13)	186.16 (27)

TABLE 4. JOINING OF 50/50 BORON FIBER REINFORCED ALUMINUM

Fasteners:	Break Fibers Require Additional Material Composite Shear Failure
Adhesives:	Adhesive Shear Failure Lacks Thermal Expansion
Resistance Welding:	Maintains Fibers 90 percent Efficient in Strength Process 13.79×10^6 N/m ² (2 ksi) 9 kib amps 0.5 second 0.635 cm (0.25 in.) diameter

welding has been the most successful way found thus far to join boron-aluminum composites. This can be done without degrading the boron fibers and the continuity of the material. Over 90 percent of the strength of the parent material can be obtained in the weld with conditions shown in Table 4. Of course, resistance welding of this type does require lap joint. This discussion is only a brief survey of the state of boron-aluminum composites, which are very promising materials.

HOT THERMAL SHIELD

The second part of this paper concerns the thermal protection of the aerodynamic surface of the

vehicle. Alloys that are typical of those planned for use and the temperature ranges in which they may be used in the Space Shuttle are shown in Table 5. These sheet materials will have to be held away from the primary structure by stand offs and fasteners. The aerodynamic surfaces themselves do not require very high strength, only good oxidation resistance and creep resistance. The stand offs or fasteners will require high strength. A metal matrix composite of TZM molybdenum wire in a matrix of Hastelloy X, a nickel alloy with chrome, iron, and molybdenum, has been shown to be a very interesting material for its high temperature strength. The strength of this composite is compared to other typical materials used at the high temperature of 1473°K (2200° F) in Table 6. The composite is superior in both strength and stiffness. Figure 3, which has been plotted in the same manner as Figure 1, is a strength-modulus map of these materials at the high temperature, and it demonstrates the superiority of the composite material. Table 7 shows that this material cannot be formed in the same manner as boron-aluminum, but the matrix must be formed as a pressed powder around the wire. The sheet is then clad in stainless steel and hot rolled. This material is not as well characterized as the boron-aluminum. It is recognized at this time that it is rather difficult to machine as most all high temperature composites are, and the joining characteristics are not well known. However, it is believed that rod and bar forms of this material can be formed into suitable high strength fasteners and stand offs to separate the hot thermal shield from the the cool primary structure of the Space Shuttle.

CONCLUSIONS

In conclusion, it should be stated that the composite materials discussed here are specialized materials currently in development, and they will be

TABLE 5. PROPOSED SPACE SHUTTLE THERMAL PROTECTION SHIELD

Prototype:		
700/922°K (800/1200° F)	Rene' 41	(Ni/20Cr/10Co/10Mo)
922/1255°K (1200/1800° F)	L605	(Co/20Cr/16W/10Ni)
1255/14 798°K (1800/2500° F)	Cb 129Y/Si Coated	(Cb/10W/10Hf)
14 798/1922°K (2500/3000° F)	Ta 222/Si Coated	(Ta/10W/2Hf)
Future:		
922/1473°K (1200/2200° F)	TZMo/Hastelloy X	(Mo/Ti/Zr) (Ni/22Cr/18Fe/9Mo)

TABLE 6. NOMINAL STRENGTH AT 1473°K (2200° F)

Density	kg/m ³ (lb/in. ³)	8857.57 (0.320)	9494.21 (0.343)	8470.05 (0.306)
Yield Strength	N/m ² × 10 ⁶ (ksi)	234.42 (34)	188.92 (27.4)	92.74 (12)
Modulus	N/m ² × 10 ⁹ (Msi)	151.68 (22)	110.32 (16)	68.95 (10)

TABLE 7. Mo/Ti/Zr WIRE REINFORCED
Ni/22Cr/19Fe/9Mo

Form:	Prealloyed Pressed Powder
Sheet:	Hot Rolled while Clad
Machine:	Difficult
Weld:	Unknown
Uses:	Fasteners and Shield

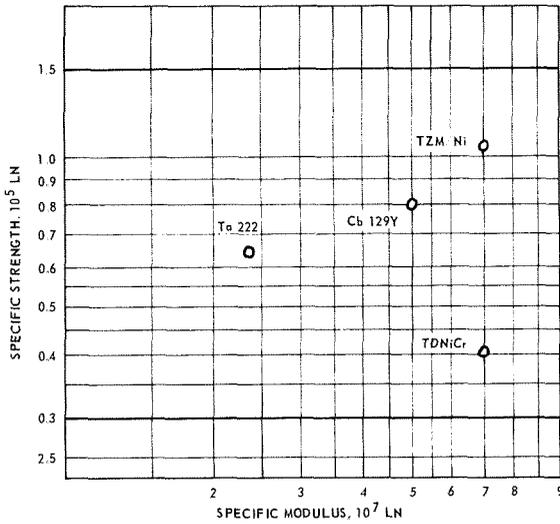


Figure 3. Strength and stiffness — density relationships for high temperature alloys at 1473°K (2200° F).

proposed only where their cost effectiveness can be demonstrated. This is based on the weight savings from their high stiffness and strength, in particular buckling resistance in uniaxially loaded components, and their compatibility with the adjoining structure. Boron-aluminum can save up to 45 percent over typical aluminum structures, while providing exceptional shear strength and joinability for a composite. Molybdenum wire reinforced nickel alloy rod can provide high strength, high temperature stand-off hardware with a weight savings of perhaps 25 percent over currently available high temperature fasteners.

HYDROGEN EMBRITTLEMENT—POTENTIAL SHUTTLE IMPACT

By

W. B. McPherson

SUMMARY

Past experience with gaseous hydrogen in high pressure ground support equipment is reviewed. The influence of hydrogen on the mechanical properties of various alloys is discussed in relation to various test variables. Possible means of forming brittle fractures in the hydrogen environment are described. Areas of the Space Shuttle that will be influenced by hydrogen are mentioned.

INTRODUCTION

Hydrogen embrittlement, as defined in this paper, is the reduction of the strength of a metal by a gaseous hydrogen environment and a change from a ductile to a brittle fracture mode. Although investigators have studied internal hydrogen for many years and the petro-chemical industry has been concerned about hydrogen at elevated temperatures, external or environmental gaseous hydrogen at room temperature has been recognized as a potential problem only recently.

HYDROGEN SERVICE EXPERIENCE

The only service failures that have been definitely diagnosed as being a direct result of gaseous hydrogen have occurred in ground support equipment. In June, 1965, a hydrogen storage vessel designed for 34.5 MN/m^2 (5000 psi) service failed at Aerojet General Corporation. This vessel, which was fabricated from A517-F (T-1) steel in the quenched and tempered condition, failed in the cylindrical section at 26.9 MN/m^2 (3900 psi) after ten pressure cycles. To examine the interior, an access was cut in the vessel head (Fig. 1). With the aid of dye penetrants, examination revealed two longitudinal cracks; one was 1.27 m (50 in.) long and the other was 0.56 m (22 in.) long. Mississippi Test Facility has three

of these A517-F steel vessels designed for 43.4 MN/m^2 (6300 psi) that were to be used for hydrogen service. In March, 1966, during a pumping delay on the second hydrogen pressure cycle, one of these vessels began to leak at 40.3 MN/m^2 (5850 psi). In the past 4 years, at least five bourdon tubes have ruptured in hydrogen pressure gauges at pressures below the rated capacity of the gauge. All the ruptured bourdon tubes were made of 400 series martensitic stainless steel. One failure, which occurred at MSFC resulted in a fire (Fig. 2). In 1969, a pressure transducer designed for 137.9 MN/m^2 (20 000 psi) service failed at MSFC. This transducer, a cross section of which is illustrated in Figure 3, was tested at 110.3 MN/m^2 (16 000 psi) with nitrogen. It failed on the first pressure cycle in gaseous hydrogen at 68.9 MN/m^2 (10 000 psi) in the top closure weld. Analysis indicates the transducer was made of 17-4 PH stainless steel. These examples of service failures in gaseous hydrogen systems illustrate that the degradation of properties by a hydrogen environment is a real problem.

EXPERIMENTAL INVESTIGATIONS

Although Bridgman reported problems with hydrogen at 9000 kg/cm^2 (882.6 MN/m^2) in steel vessels [1], only a few investigations [2-6] on metals in gaseous hydrogen (GH_2) at room temperature had been made when the NASA's pressure vessels began to fail. None of the alloys in hydrogen service had been evaluated in a GH_2 environment, so immediate work was begun to study the steels used to construct pressure vessels.

Smooth and notched cylindrical specimens were used to evaluate the tensile properties of different alloys in a $68.9 \text{ MN/m}^2 \text{ GH}_2$ environment. The influence of the test environment is more readily observed by a reduction of strength in the notched tensile tests. As illustrated in the plot of yield strength in air versus the reduction of notched strength in $68.9 \text{ MN/m}^2 \text{ GH}_2$ as compared to

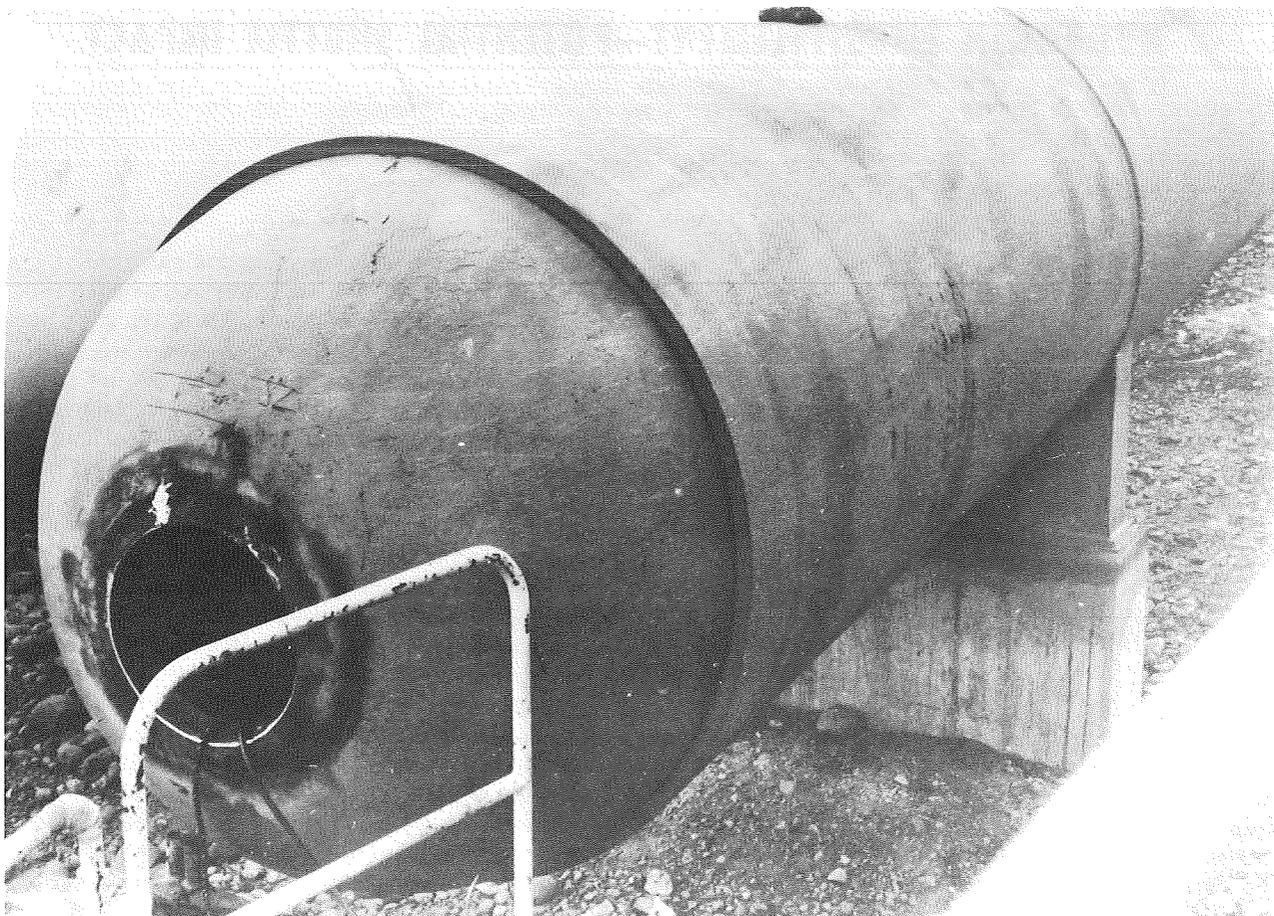


Figure 1. View of failed A517-F steel vessel showing access cut for inspection.

68.9 MN/m² helium (Fig. 4), the degree of embrittlement generally increased as the strength of the alloy increases. Alloys could be classified as severely embrittled, including the high strength steels and high strength nickel alloys; moderately embrittled, covering the structural steels, pure nickel, and titanium alloys; and slightly embrittled, including pure titanium, nonstable austenitic stainless steel, and beryllium copper. Hydrogen had almost no influence on stable austenitic stainless steel, precipitation hardened austenitic stainless steel, aluminum alloys, and OFHC copper.

In the beginning of this work, it was assumed that hydrogen diffusion was necessary to create embrittlement, and, thus, the test would have to be time dependent. Several alloys were exposed to 68.9 MN/m² GH₂ for long periods with a sustained tensile load equivalent to 75 percent of the yield

strength, and tested to failure in the environment at the end of the hold period. The results of the tests are illustrated in Figure 5 for A302-B steel. The smooth specimens had about the same strength after 100 days as the test in helium. The decrease in strength is more apparent in the notched specimens. Although there is an initial loss of strength as compared to the helium test, nearly half of this reduction is recovered after 100 days. This recovery, however, is the result of strain aging. (Strain aging is a phenomenon that occurs in steels held under load for periods of time to permit carbon to diffuse to favorable crystallographic sites thereby hindering dislocation mobility.) Notched specimens tested as soon as the chamber reached test pressure, that is at zero hold time, had the greatest reduction in strength. 6Al-4V titanium also had a substantial reduction of notch strength with zero hold time. It became evident that embrittlement and degradation of properties were not time dependent.

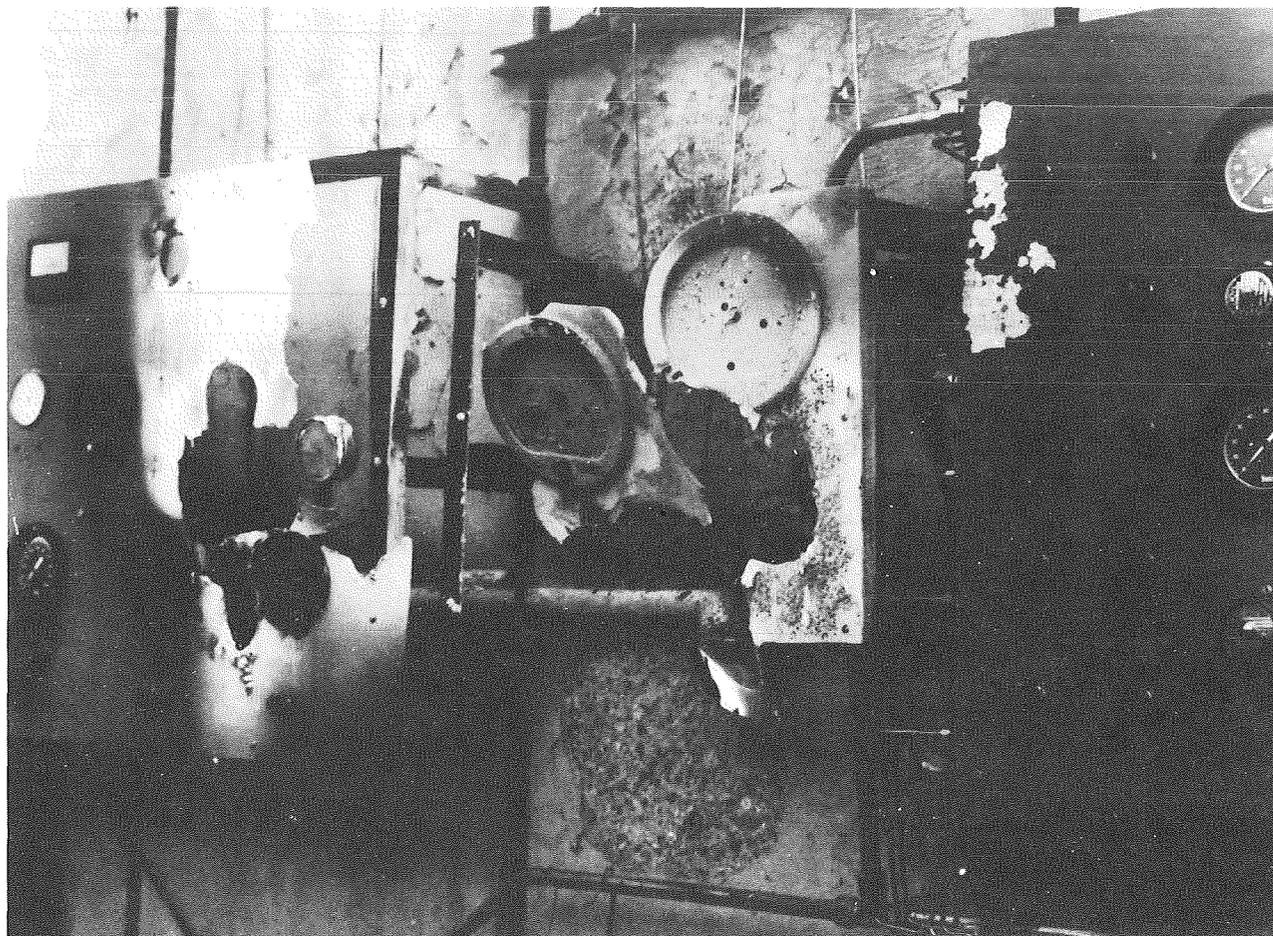


Figure 2. Area damaged by hydrogen fire as a result of a bourdon tube failure.

As illustrated in Figure 6 for Inconel 718 nickel, the degree of embrittlement is pressure dependent. The influence of pressure is related to both alloy and strength, since, for example, the high strength steels have a greater reduction in strength at low pressures than the lower structural steels.

Most tests have been made at room temperature. Thus far, only two alloys, 6Al-4V titanium and Inconel 718 nickel, have been tested at low temperatures, and no alloys have been tested at elevated temperature. Below room temperature, the influence of GH_2 on property degradation decreases as the temperature decreases to about 88.7°K (-300°F) at which point the GH_2 environment ceases to influence strength. This is illustrated for 6Al-4V titanium in Figure 7. It would be inappropriate to speculate on the influence of elevated temperatures.

As is usual in the case of an aggressive environment, GH_2 reduces the fatigue strength. From Figure 8, GH_2 on Inconel 718 seems to have a greater influence on fatigue at lower stress levels. Insufficient tests have been completed to regard this as a general trend. It is interesting to note that the tests in air and those in 0.69 MN/m^2 (100 psi) GH_2 are about the same, which is somewhat less than helium. This is consistent with the results of fatigue tests in reduced pressure and inert environments [7] in which the lower fatigue strength has been obtained in an air environment. Thus, the evacuation-purge procedure used in this investigation to clean the specimens and chamber before running the test is apparently satisfactory.

Cyclic crack growth as depicted in Figure 9 for 6Al-4V titanium is greater in the GH_2 environment even at 0.101 MN/m^2 (1 atm) pressure than in

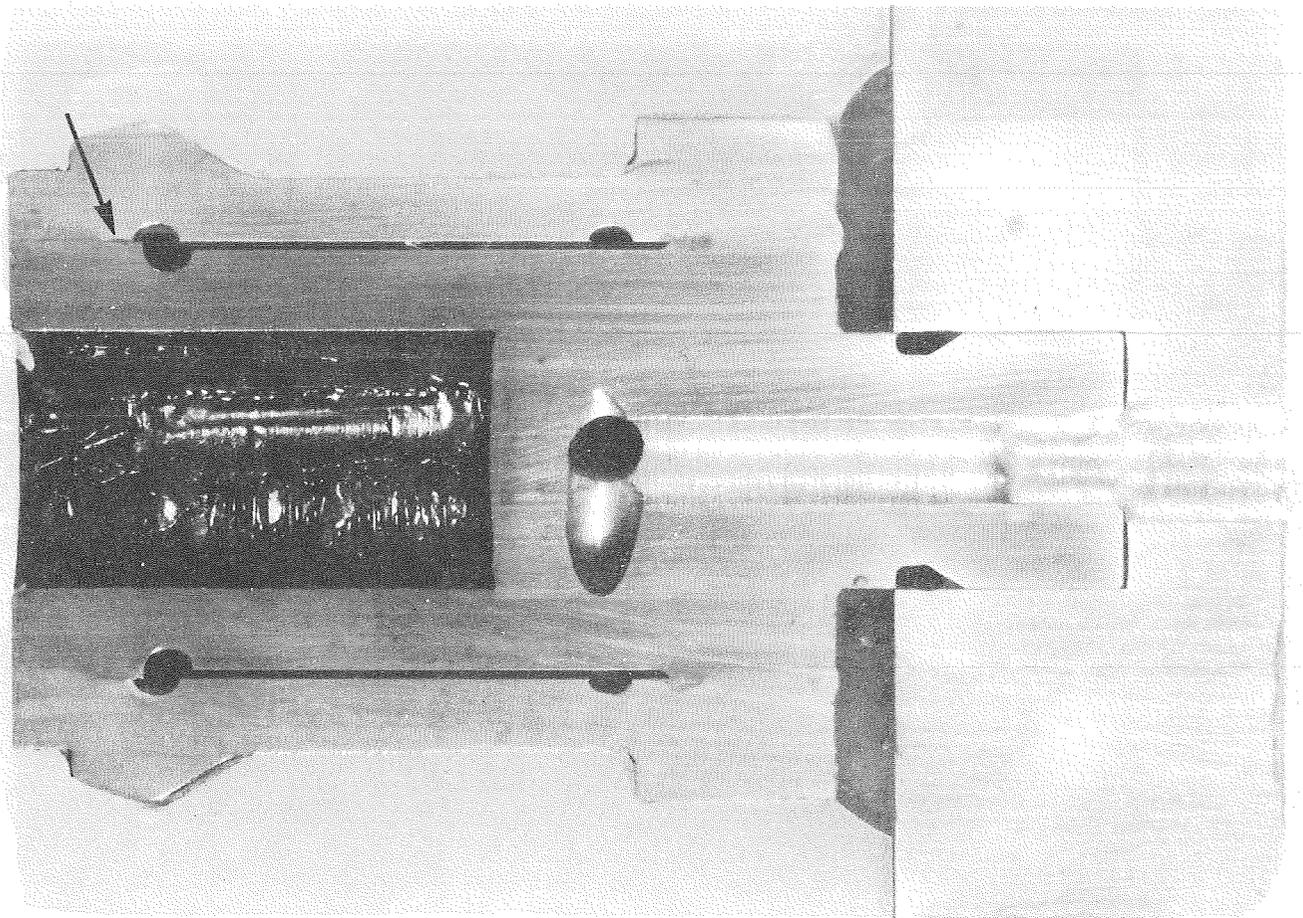


Figure 3. Cross section of a failed pressure transducer. [Failure occurred in weld (arrow).]

helium. There is less variation in crack growth at low cycles, which implies that the crack initiation period is not greatly influenced by the environment.

Crack growth can be inhibited by oxygen [8] as illustrated in Figure 10; of course, oxygen is generally not desirable in a GH_2 system. This suggests however, the possibility of discovering a coating that might inhibit the hydrogen. Even in a humid environment (Fig. 11), crack growth is still substantial [8] though not as great as in pure GH_2 . Such a hydrogen rich humid environment would likely occur in the combustion chamber of an LH_2 -LOX rocket engine and could be a potential problem from the standpoint of crack growth.

CRACK FORMATION

The most noticeable characteristic of smooth specimens tested in a GH_2 environment is surface

cracks that have developed on 304 stainless steel as illustrated in Figure 12. One such crack leads ultimately to failure. A typical fracture of a ductile material in a non-aggressive environment, as illustrated by the nitrogen test of 304 stainless steel at the same pressure, shows a measurable reduction in diameter and a completely ductile fracture. On the other hand, the GH_2 test has almost no change in diameter, and the initial crack area has the appearance of a brittle fracture with only the final phase in shear. Surface cracking has been found only above the yield of the metal. Specimens strained within the elastic range of the material have been removed from the environment and tested in air without any crack formation or degradation of properties. Thus, to have this type of environmental embrittlement, the metal must be in the GH_2 environment at the time the plastic strains are applied. This does not mean a structure would be safe in the elastic range. At points where notches and discontinuities occur, if the geometry is sufficiently severe, the metal can yield at the root of a notch while the mass surrounding

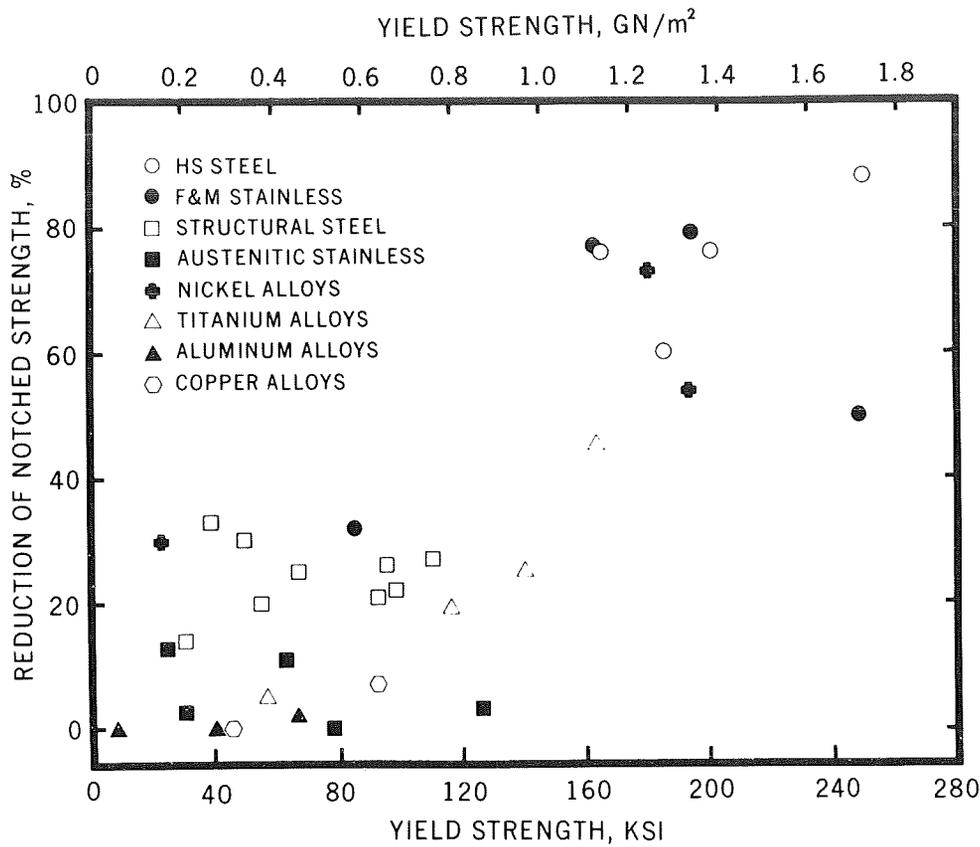


Figure 4. Yield strength in air versus reduction of notched strength in 68.9 MN/m² (10 000 psi) hydrogen.

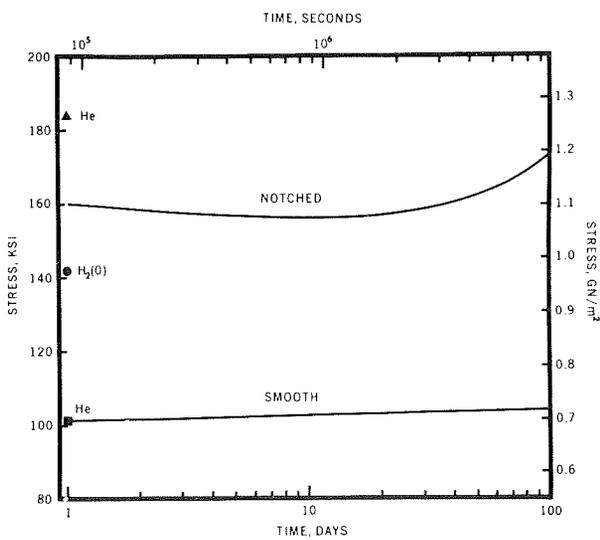


Figure 5. Influence of time on the strength of A302-B steel in 68.9 MN/m² (10 000 psi) hydrogen.

it is still elastic. Therefore, a crack will develop early and propagate at a notch. The oxide film on the surface of the metal acts as a natural barrier to the hydrogen. As the metal enters the plastic range, crystalline slip occurs at the surface, ruptures the oxide film, and exposes fresh metal to the hydrogen environment. At this point, the hydrogen apparently "damages" the metal. One possible mechanism by which the hydrogen can embrittle the metal is analogous to Westwood and Associates' [9] explanation of liquid-metal embrittlement. As a force F (Fig. 13) increases, a crack will propagate, either by cleavage or shear depending on which mode operates first, tensile stress (τ) of the bond A-A at the crack tip or shear stress (σ) on the most favorably oriented slip plane. Chemisorption of the hydrogen (black dot) at the bond between the atoms A-A will reduce the tensile stress. If the adsorbed hydrogen does not influence the metal more than a few atom diameters from the crack tip, it is not likely to change the strength across the slip plane, and the shear stress will not be greatly changed. This theory agrees with tensile tests in that no

change in yield strength has been observed. Thus, if the adsorbed hydrogen reduces tensile stress without altering the shear stress, the metal will tend to fail by cleavage in a brittle manner rather than by slow, ductile shear.

A second mechanism might be hydrogen absorption or diffusion. Hydrogen diffusion has been studied by investigators for many years without

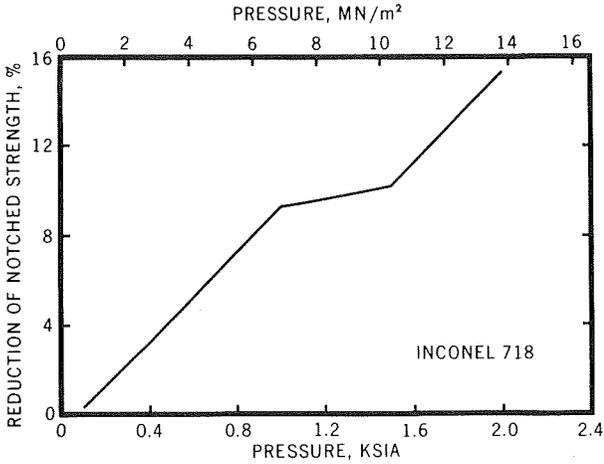


Figure 6. Influence of hydrogen pressure on the reduction of notched strength of Inconel 718 nickel.

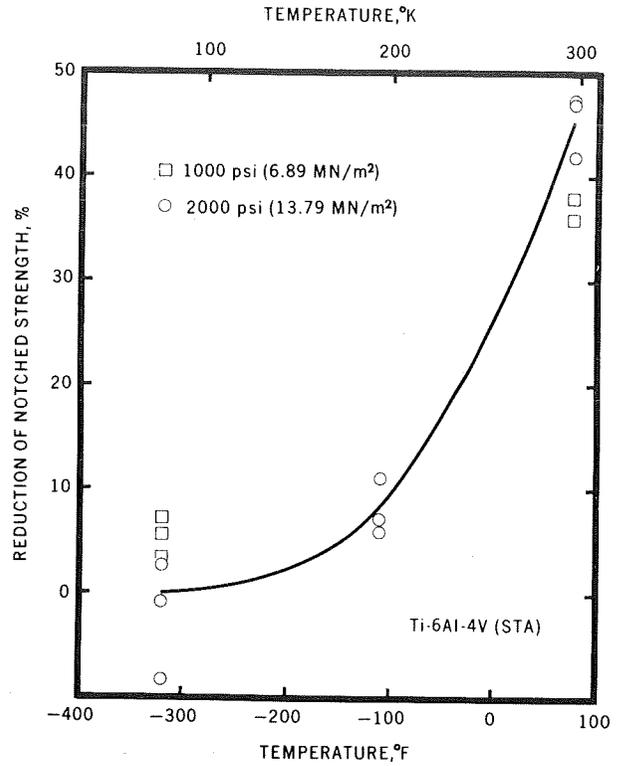


Figure 7. Influence of temperature on the reduction of notched strength of titanium 6Al-4V (STA).

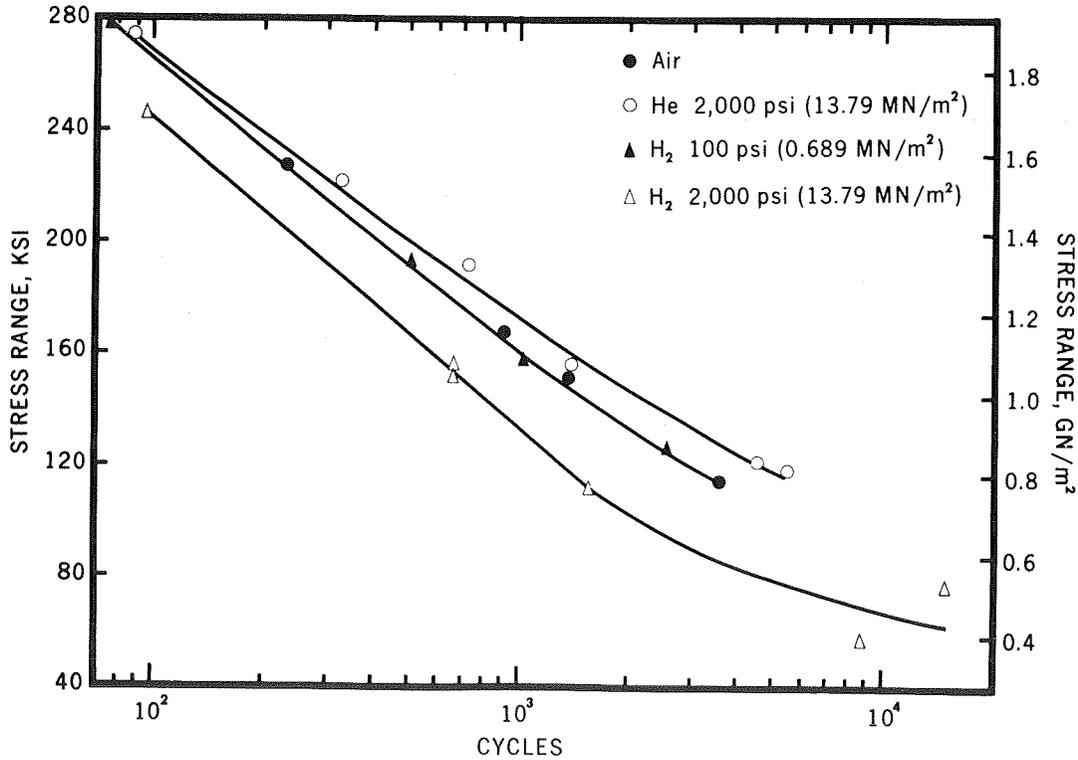


Figure 8. Reduction of low cycle fatigue strength of Inconel 718 nickel by hydrogen.

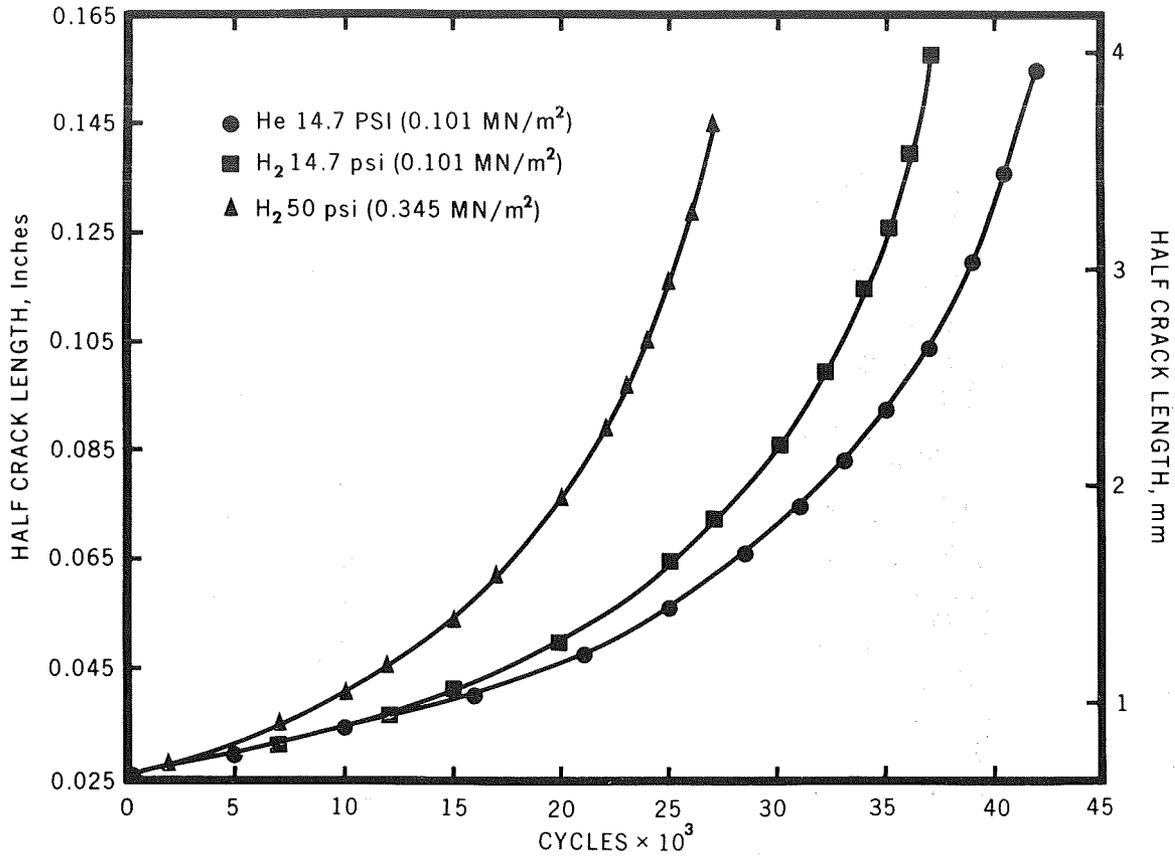


Figure 9. Influence of hydrogen on crack growth in titanium 6Al-4V (STA).

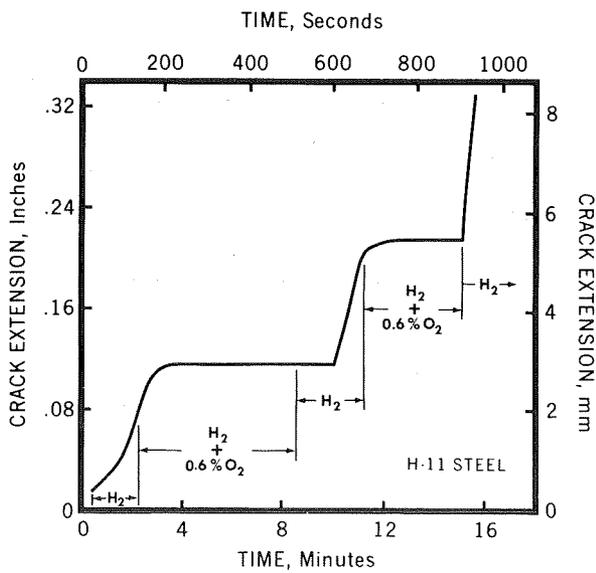


Figure 10. Crack growth in hydrogen and hydrogen-oxygen mixtures of H-11 steel [8].

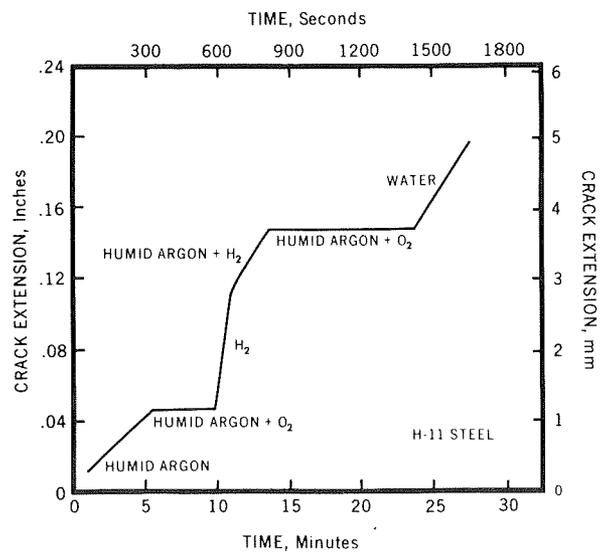


Figure 11. Crack growth in various humidified environments in H-11 steel [8].

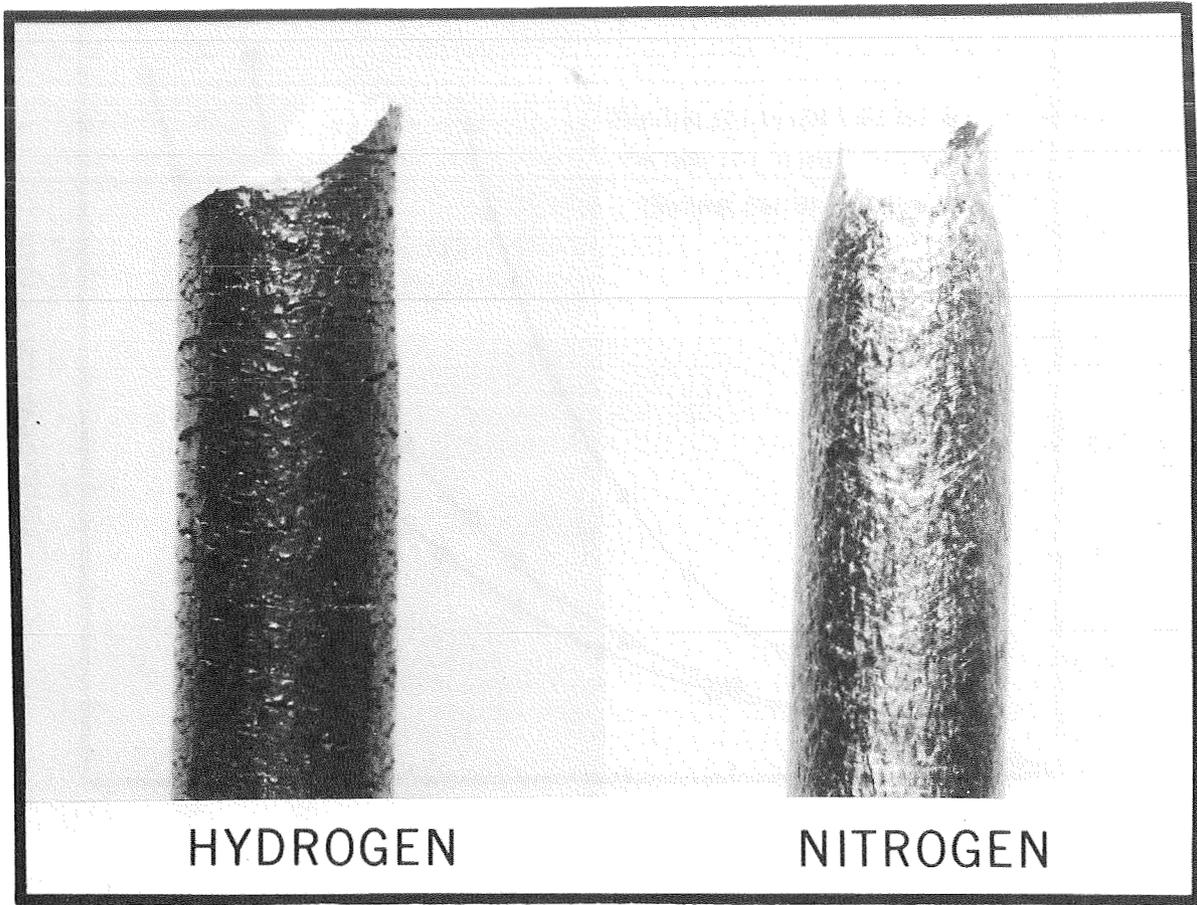


Figure 12. Surface cracks formed on 304 stainless steel tested in hydrogen.

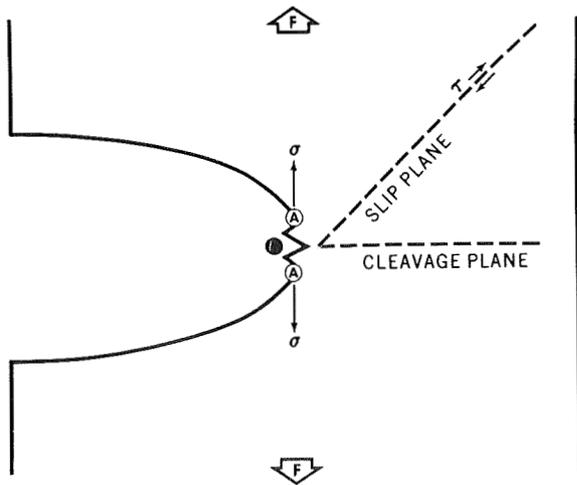


Figure 13. Schematic of a crack in a solid [9].

arriving at a fully satisfactory explanation for its relation to embrittlement of metals. In the case of external hydrogen, the short time between yield and fracture of a tensile specimen would restrict the diffusion to a few lattices ahead of the crack. The absorbed hydrogen might hinder dislocation motion, thereby preventing slip from occurring and, thus, reducing the ductility. This does not leave a satisfactory explanation for the reduction in tensile strength and may, therefore, require both adsorption and absorption as a third possible mechanism. In any case, it is obvious that much more research is needed to clarify hydrogen embrittlement.

CONCLUSIONS

The influence of GH_2 has been described in this paper as a manifestation of property reduction, or degradation, and metal failure in a brittle mode,

and occurs only when the environment is present. Present information of the Space Shuttle indicates that high pressure hydrogen propulsion systems will be used in long life flight vehicles. With few exceptions, the high strength alloys that would normally be used in the construction of such a vehicle are influenced by the hydrogen environment. Obviously, all of these alloys can not be dismissed because of the potential problem associated with hydrogen. Therefore, design parameters for each alloy in the

environment must be developed to permit application in the hydrogen system of the Shuttle. Two useful parameters are the threshold stress intensity, K_{TH} , and low cycle fatigue. From this information, design stresses can be established such that cracks or flaws not detected by inspection will not grow to a critical size during the expected life of the Shuttle. The areas in which a hydrogen environment is in contact with a metal surface must be scrutinized to assure the reliability for which the Shuttle is being designed.

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DEVELOPMENT OF FUEL TANK SEALANTS FOR ADVANCED HIGH PERFORMANCE AIRCRAFT

By

W. J. Patterson and L. R. Moffett

SUMMARY

This review describes the current studies directed toward the development of a polymeric material capable of functioning as a fuel tank sealant in hypersonic aircraft. The preparation of a number of organic intermediates is outlined that encompasses a variety of systems including aryl-fluorinated compounds and aromatic polycyclic structures. Preliminary results indicate that incorporation of fluorine atoms into the basic polymer structure imparts a degree of aviation fuel resistance, a property that the sealant must possess. The rationale supporting the selected polymeric systems chosen for study and investigation is outlined along with other pertinent factors involved in the selection of candidate materials. The Monsanto Research Corporation of Dayton, Ohio, under NASA contract, has been engaged in supplemental studies involving the development of thermally resistant polymers as fuel tank sealants. This program has been designated Task A and is an integral part of a three-phase contracted system designed to provide a workable polymeric sealant for hypersonic aircraft. The efforts of Tasks A as well as Tasks B and C, also under NASA contracts to Monsanto Research Corporation and Battelle Memorial Institute, Columbus, Ohio, respectively, are outlined within the body of this report.

INTRODUCTION

Marshall Space Flight Center has undertaken the development of a new generation of polymeric sealants for fuel tanks on hypersonic aircraft such as the supersonic transport (SST). This type of technology would be extendable to the Space Shuttle program if a decision is made to use kerosene-air breathing engines in any capacity. The critical problem

associated with fuel tank sealants in the SST-type aircraft is shown in Figure 1.

Figure 1 shows the largest proportion of fuel tankage is housed in the wing structure, and is subject to a range of aerodynamic heating. The specific areas of concern are outlined as follow:

1. High cruise speed/wing skin temperatures of 505 to 533°K (450 to 500° F).
2. Half of fuel capacity in wing tanks — fuel vapor temperatures up to 505°K (450° F) in flight.
3. Fuel has high aromatic content.
4. Wing flexure at subzero temperatures during taxi and climb-out.

The high cruise speed of the aircraft will generate skin temperatures of at least 505°K (450° F) on the leading edge, and since the fuel tanks are located predominantly in the wings, the tank sealants will be exposed to the fuel at severe temperatures, which would normally be a degrading environment for a polymeric material. To make the problem more severe, the aromatic components in the fuel are excellent solvents for most organic polymers. In addition to the high temperature requirement, the sealants must accommodate normal wing flexure during cold ground conditions. This requires a large elastomeric response range for the sealant. With these problems in mind, the MSFC program was initiated to develop a polymeric sealant suitable for SST fuel tank applications.

Specific material requirements were used as goals of the program, as summarized in Table 1. The sealant must withstand these thermal and fuel environments for periods of 20 000 to 25 000 hours, approximating aircraft service life of 50 000 hours. It is desirable in terms of weight saving to omit

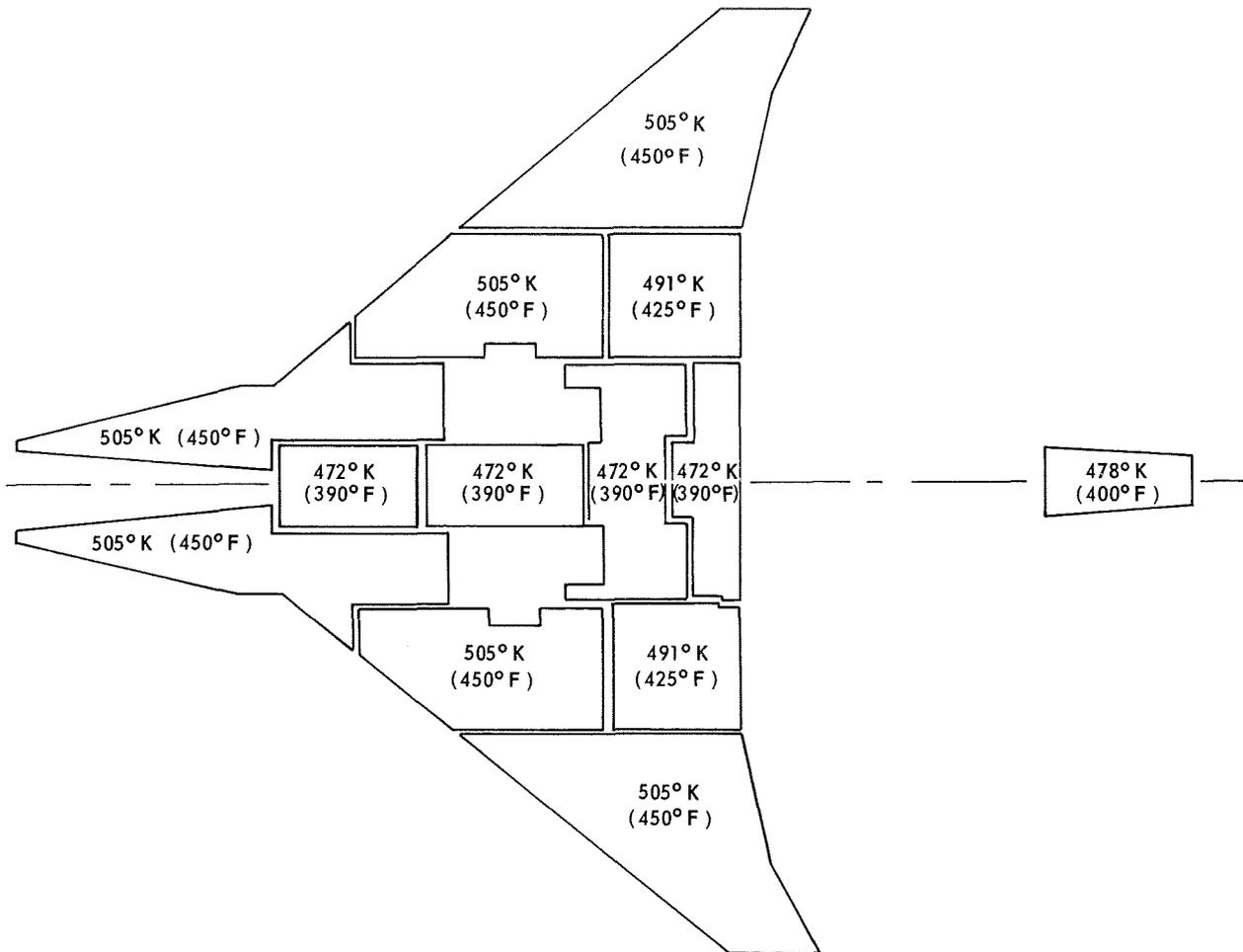


Figure 1. SST fuel tank locations and temperature distributions.

TABLE 1. SEALANT PROPERTY REQUIREMENTS

<p>Thermal Stability: Inherent Stability to 533° K (500° F) for Extended Periods of time</p>
<p>Fuel Resistance: Not Degraded at 533° K (500° F) by Hydrocarbon Fuels</p>
<p>Environmental Conditions: Above Requirements under Oxidizing Environment</p>
<p>Adhesion: Minimum Bond Strength to Titanium Alloys of 3.45×10^6 N/m² (500°psi) (Shear) and 2679 gm/cm (15 lb/in.) (Peel)</p>
<p>Titanium Compatibility: No corrosion of Stressed Titanium Alloys at 533° K (500° F).</p>

inerting systems from the wing tanks, so the sealant should have adequate oxidative resistance. Obviously, a minimum adhesion of the sealant is required to preclude fuel leakage. The anticipated use of highly fluorinated sealants has introduced the problem of stress corrosion of the 6Al-4V titanium alloy and has become one of the basic requirements of the program.

A basic polymer development effort was thus initiated in-house to produce a sealant material that would satisfy these requirements. A series of contracted efforts designated as Tasks A, B, and C were then started to supplement the in-house effort. The overall program coordination is outlined in Figure 2.

The predominant in-house effort as well as that of Task A is directed toward new, highly fluorinated sealant polymers since this type of structure has inherently high fuel resistance and thermal stability.

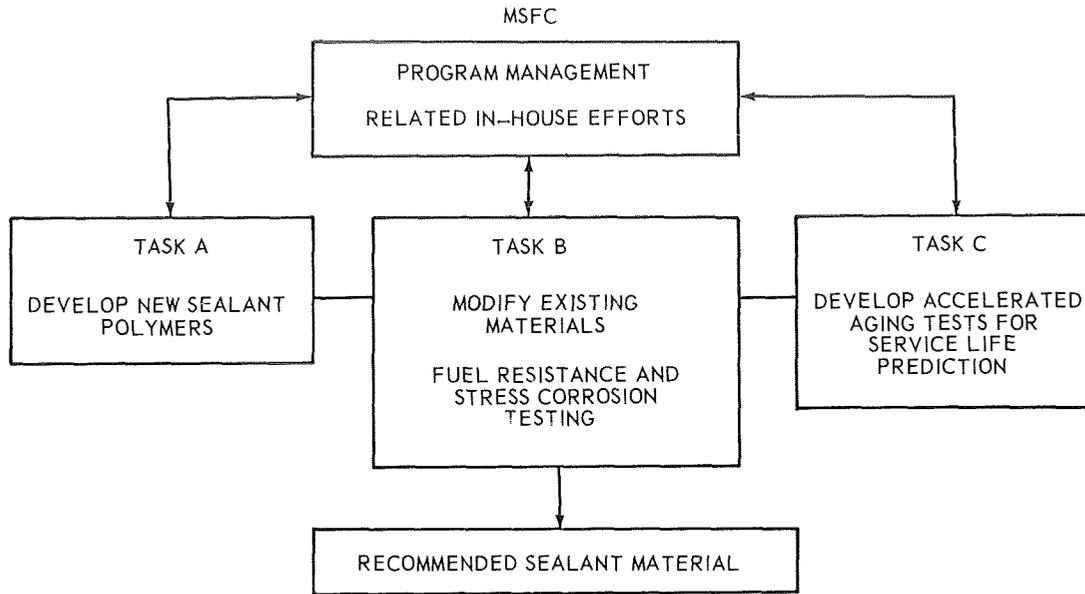
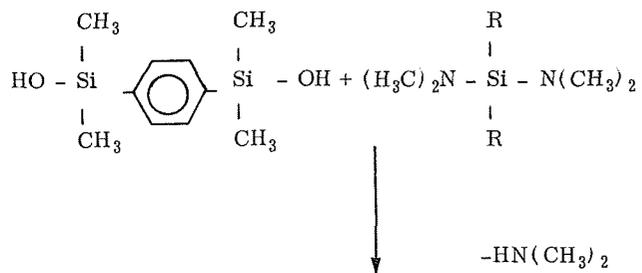


Figure 2. Total MSFC sealant program.

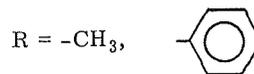
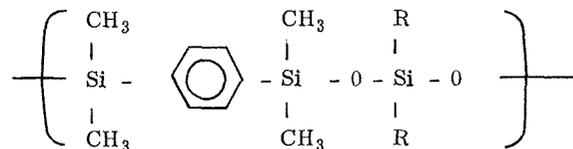
Task B is concerned with the modification and evaluation of commercial materials, particularly in terms of hydrocarbon fuel resistance and titanium stress corrosion. It serves also as the proving ground for new polymers from the in-house or Task A efforts. Task C is a more fundamental study to develop short term evaluation techniques using critical sealant parameters that will reliably predict the long term service life of the sealant up to 50 000 hours.



DISCUSSION

MSFC In-House Program

The in-house sealant development program has been oriented primarily toward a new class of aromatic silicone polymers that will be termed silphenylene-siloxanes. A general representation of this polymer is shown in Figure 3. This polymer can be prepared by the illustrated condensation process in weight-average molecular weights up to 500 000. Elastomers having high strength and thermal stability are formed by cross-linking this polymer. Figure 4 compares the isothermal aging characteristics of the experimental polymer with conventional silicones, which are the closest commercial counterpart. To improve the fuel resistance of these polymers, a large proportion of fluorine is being incorporated, and a series of monomers have been prepared



Polymer is Viscous Oil with n_{inh} up to 0.9

Figure 3. Silphenylene - siloxane polymers.

that contain varying degrees of fluorination as depicted in Figure 5.

This series of flourinated aminosilanes was prepared by the general synthetic method outlined in

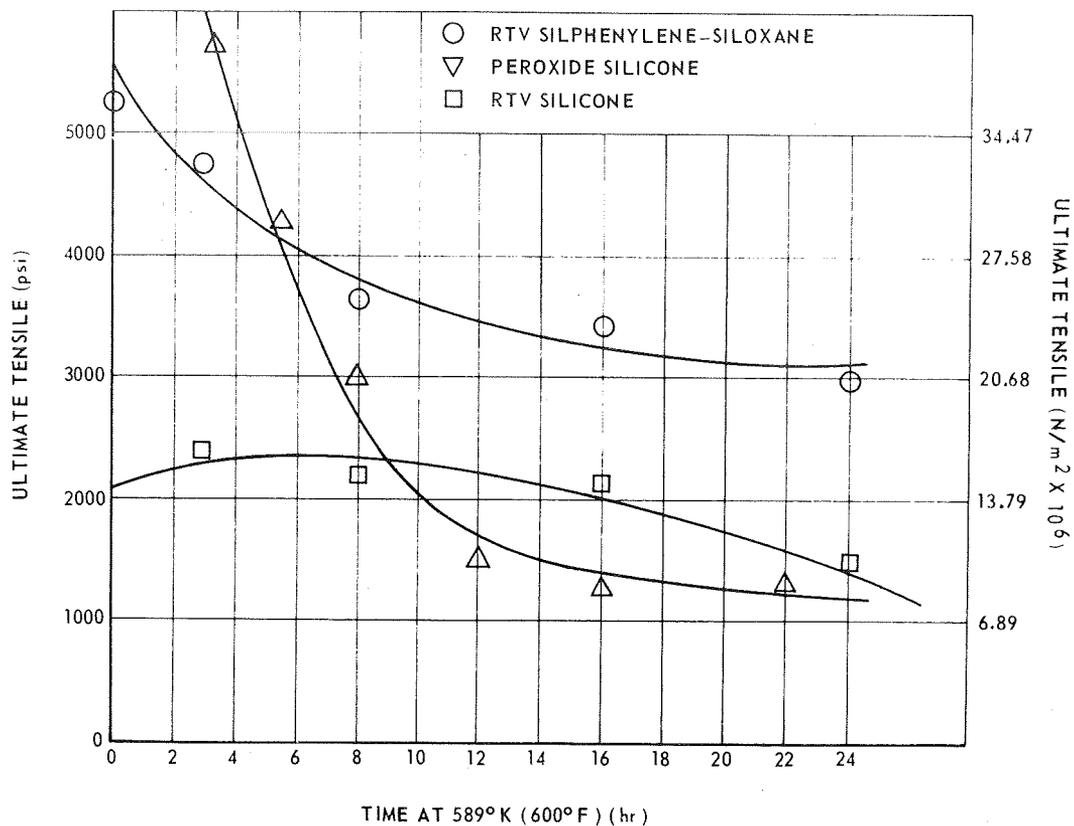


Figure 4. Thermal stability of silphenylene-siloxane.

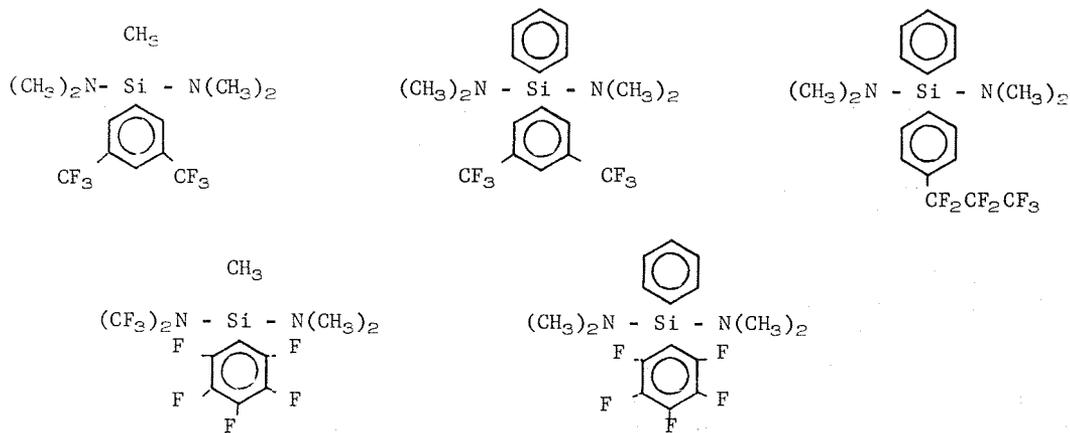


Figure 5. Fluorinated aminosilanes.

Figure 6. In the approach shown in Figure 6, a Grignard reagent is prepared from the fluorinated group and is then condensed with the appropriate silicon alkoxide. The resultant compound is chlorinated and finally dimethylaminated to yield the

monomer in a form suitable for polymerization. Low molecular weight polymers have been prepared from most of these intermediates which, when cured, had significantly greater fuel resistance than their unfluorinated counterparts. However, a higher

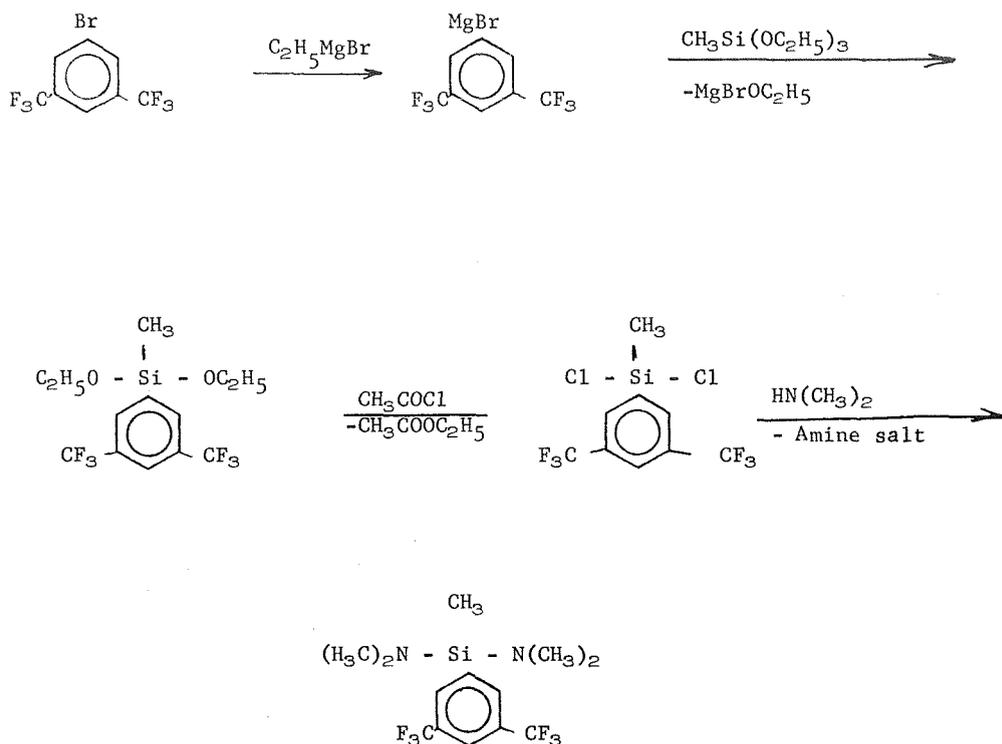


Figure 6. Synthesis of fluorinated intermediates.

degree of fuel resistance was required, and additional methods have been developed to incorporate fuel resistant moieties. Intermediates containing two highly fluorinated groups could be prepared by the method shown in Figure 7. The preparation of the diisopropoxysilane intermediate using the first step of this sequence proceeded normally, but the normal chlorination and amination steps could not be carried

out. Instead, the intermediate in the dialkoxide form has been converted to the diol for subsequent incorporation into the silphenylene polymer, as visualized in Figure 8. The diol shown in Figure 8 has been prepared and tentatively characterized. Efforts are proceeding to prepare a larger quantity of this diol for incorporation into the polymer structure.

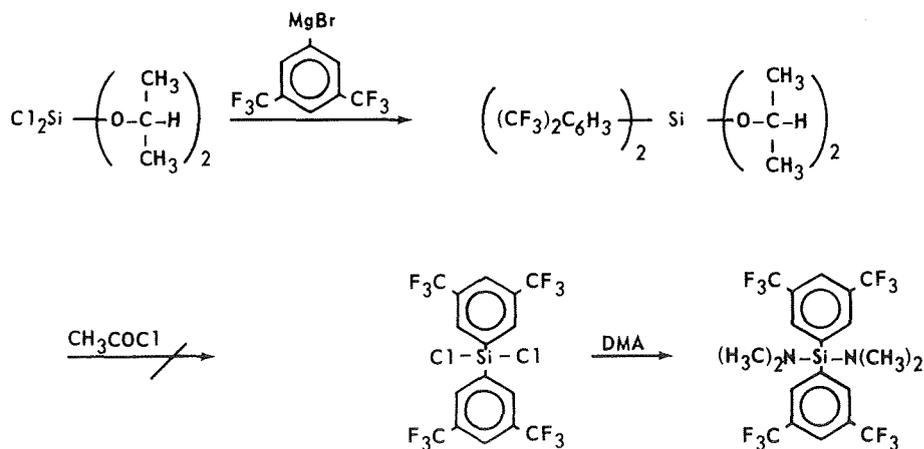


Figure 7. Preparation of highly fluorinated intermediates.

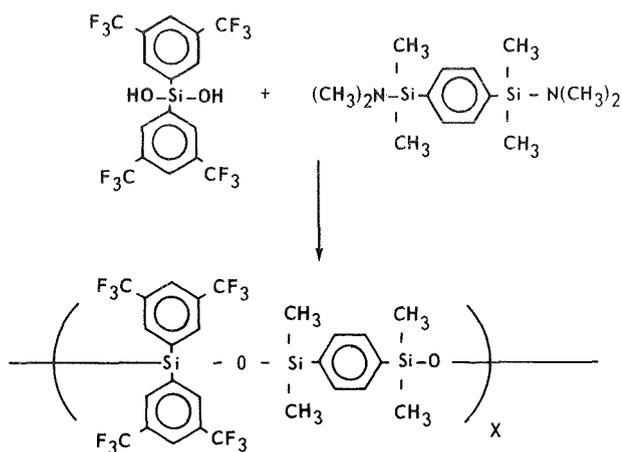


Figure 8. Fluorinated silphenylene-siloxane polymer.

Other approaches have been studied where either fluorination or higher aromatic content is present in the diol monomer. One such approach is outlined in Figure 9. This involves an initial Ullman-type coupling reaction in the presence of activated copper in an aprotic solvent to yield the dibromide. The Grignard reagent is readily formed and, in the presence of dimethylchlorosilane, yields the dihydride. This is carefully hydrolyzed with $\text{CH}_3\text{OH}/\text{NaOH}/\text{H}_2\text{O}$ to yield the desired diol. Several diol intermediates currently under study are shown in Figure 10. Compound III was prepared from 1,4-dibromonaphthalene by the procedure outlined in Figure 9. Compound IV has not been successfully synthesized to date. Compound II is commercially available and has been

utilized as well as I and III to form linear polymers depicted in Figure 11. The cured polymers from (1) and (2) of Figure 11 were tough elastomers that are currently being evaluated for fuel resistance. Only low molecular weight polymers having the form of (3) have been obtained to date, and higher molecular weight materials are currently being sought.

Contracted Programs

TASK A (MONSANTO RESEARCH CORPORATION)

The predominant synthesis effort in the Task A program has involved a class of polymers termed polyperfluoroalkylarylisocyanurates. This approach takes advantage of the adequate thermal stability and curing characteristics inherent in the isocyanurate polymer. A series of intermediates leading to the desired polymer has been prepared as described in Figure 12. This synthesis involves an Ullman-type coupling to form the dinitro intermediate, followed by reduction and phosgenation to yield the desired diisocyanate. These intermediates have been polymerized either with *m*-trifluoromethylphenylisocyanate or alone to form a tough cross-linked isocyanurate as shown in Figure 13. This cyclic trimerization occurs readily at modest temperatures, and the polymers incorporating the $(\text{CF}_2)_x$ linkages are fuel resistant although not elastomeric. The perfluoroalkyl ether polymer shown in the figure would provide elastomeric character to the polymer. It is commercially available, and synthesis methods for its incorporation into the isocyanurate polymer backbone are presently being

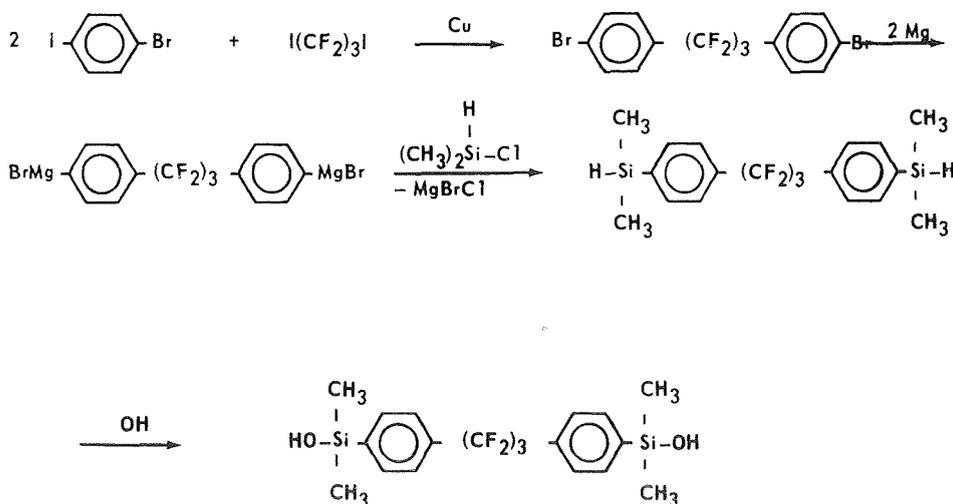


Figure 9. Ullman coupling reaction.

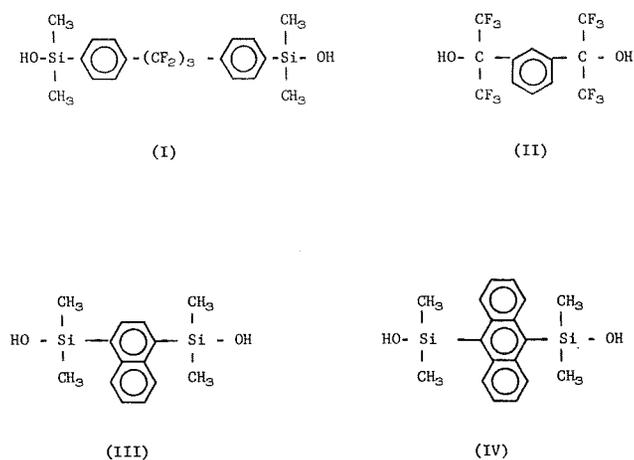


Figure 10. Experimental diol intermediates.

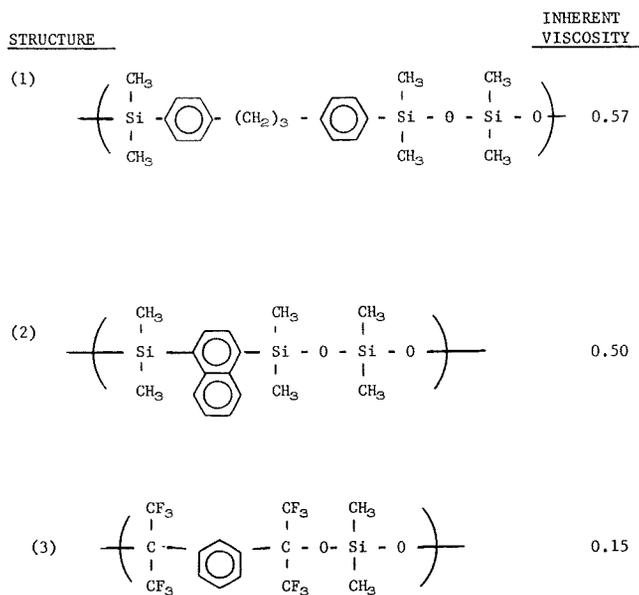


Figure 11. Candidate sealant polymers.

worked out. One of these methods involved an initial Friedel-Crafts acylation as shown in Figure 14. This step is followed by nitration, reduction, and phosgenation. This sequence has been verified using model compounds, and a quantity of the perfluoroalkylether prepolymer has been obtained for preparation of the isocyanate-terminated prepolymer.

As an adjunct to the Task A effort, a study of modified heterocyclic polymers is being carried out by Quantum, Incorporated. The original requirement for an elastomeric sealant remains as the prime approach, but the utility of a higher modulus sealant

material is being examined as an alternate approach. The heterocyclic polymers such as the polyimides are particularly attractive in view of their inherent thermal stability and fuel resistance. Thus, this effort is oriented toward incorporation of a propylene ether prepolymer into the polyimide backbone as illustrated in Figure 15.

This structure represents a terpolymer prepared from an aromatic diamine, a dianhydride, and an amine-terminated, propylene ether prepolymer. The specific objective is to incorporate a sufficient quantity of the prepolymer to confer some resilience or elastomeric character to the polymer without a significant sacrifice in thermal stability or fuel resistance. Several variations of this formulation have been prepared, and preliminary evaluations indicate that it may be adaptable to the sealant application.

TASK B

Task B of the overall three-part program encompasses the formulation and evaluation of improved thermally resistant sealant materials for use in hypersonic aircraft fuel tanks. Contractual assistance has been obtained for this task from Monsanto Research Corporation. Task B is entitled "Processing, Application, and Evaluation of Sealants for Fuel Tanks in Advanced Aerospace Structures." This task has two main objectives: to determine what influence various fluorinated molecular structures have on the stress corrosion susceptibility of Ti-6Al-4V; and the formulation, application, evaluation, and process engineering of new sealant materials for possible use in the fuel tanks of advanced high speed aircraft. An important function of this task was to determine unequivocally if fluorinated polymers, regardless of structure, inherently enhance this stress corrosion, or if the phenomenon is completely dependent on polymer structure of configuration. To this end, four fluorinated structures were selected for evaluation as shown in Figure 16.

In the selection of candidate high temperature fuel tank sealants, it had been anticipated that the sealant materials developed under Task A would be available for testing in the latter part of the program. However, this did not materialize, and there was no success in obtaining samples of high temperature sealants in the advanced state-of-the-art that offered promise for use in high speed aircraft; namely, carborane-siloxane polymers, perfluoroalkylene triazines, and perfluoroalkylene oxides cured with triazines.

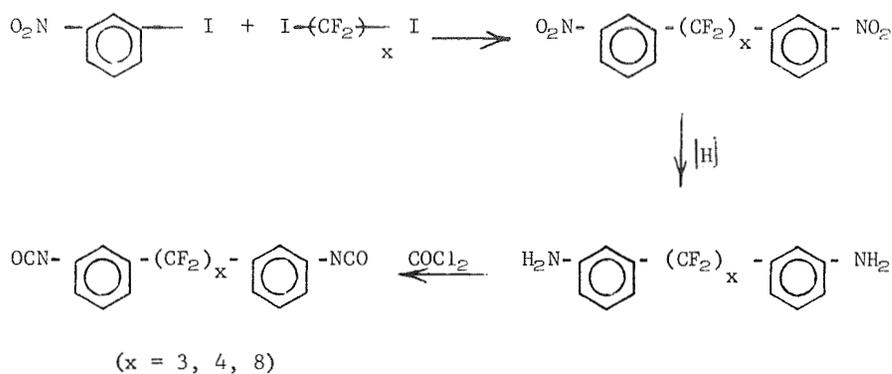
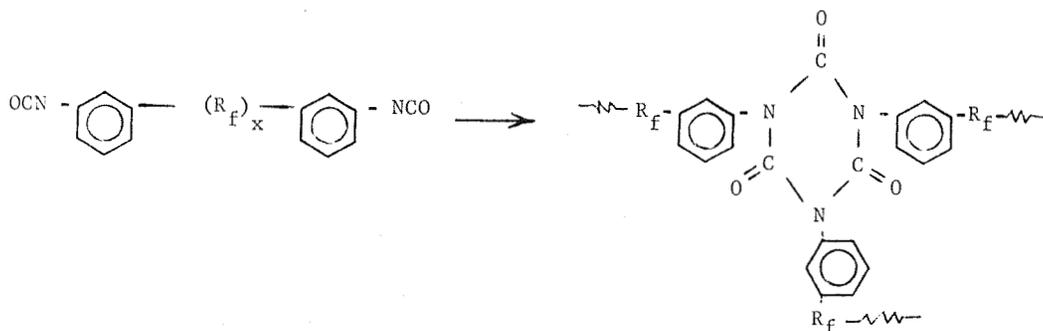


Figure 12. Isocyanurate polymer precursors.



Where $R_f = (\text{CF}_2)_x$,

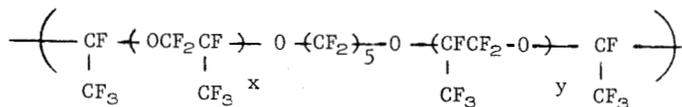
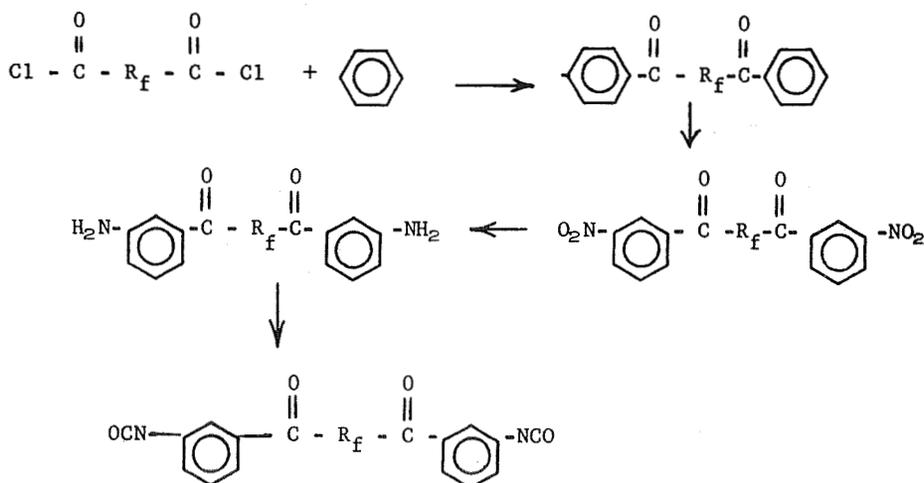


Figure 13. Fluorinated isocyanurate polymers.



Where $R_f =$ Perfluoroalkylether Prepolymer.

Figure 14. Synthesis of isocyanate-terminated prepolymer.

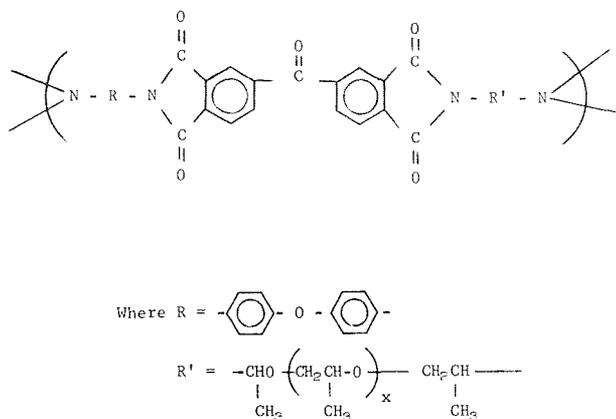
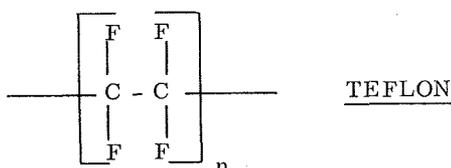
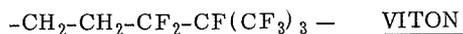


Figure 15. Modified polyimide sealants.

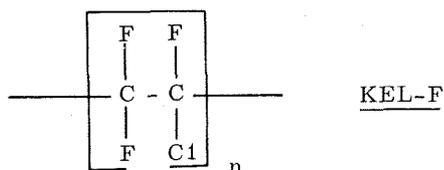
1. A HIGHLY FLUORINATED COMPOUND



2. A PARTIALLY FLUORINATED COMPOUND



3. A FLUOROCHLORO COMPOUND



4. A FLUORINATED SILICONE

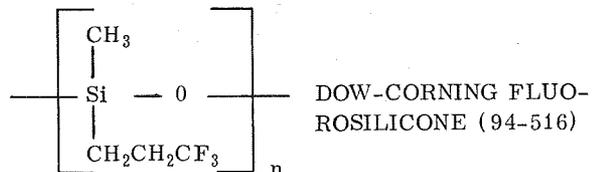


Figure 16. Candidate commercial sealants.

Initial sealant evaluation was therefore performed with the Viton and Dow-Corning fluorosilicone 94-516 sealants that had been procured for the stress corrosion study. Dow-Corning also submitted two one-part fluorosilicone sealants, Nos. 94-030 and 94-002, and these were evaluated. Late in the program the Air Force Materials Laboratory at Wright-Patterson Air Force Base submitted two of their best Viton sealants for testing. One was based on Viton B and Viton LM, and the other was based on Viton C-10.

Sealants were initially evaluated by exposing them to 533°K (500° F) vapor of JP-4 and MIL-J-5161 Referee Grade II fuels for 70-hour periods. A typical sealant formulation that was evaluated during the course of the program is shown in Table 2. A summary of average lapshear data for several candidate sealants that had been exposed to 533°K (500° F) fuel vapor for 70-hour periods is shown in Table 3.

As can be noted, all the evaluated sealants degraded somewhat after 70 hours of exposure, but the fluorosilicone sealant 77-028 and a sealant based on Viton C-10 both retained lapshear strengths near the specified minimum of 3.45×10^6 N/m² (500 psi).

The stress-corrosion studies with the four structurally different fluorinated polymers were made at 533°K (500° F) only, since halogenated salts have been shown to produce stress corrosion at a minimum temperature of 505°K (450° F). Post-exposure examinations were made for sealant swell, cracking, debonding, and increased brittleness. The specimens that had not failed under sustained load were then loaded to failure on an Instron testing machine to determine whether any embrittlement occurred or actual stress corrosion cracking had commenced.

Table 4 shows the results of the long term compatibility at 533°K (500° F) between Ti-6Al-4V and various fluorinated sealants.

Although two specimens that were exposed to the Kel-F material at 533°K (500° F) did not fail after 1000 hours, post-exposure tensile testing revealed significant cracking had been induced by the Kel-F. The room temperature tensile strength was reduced by 55 percent, and the 533°K (500° F) strength was reduced by 53 percent. Specimens exposed to Teflon and the Dow-Corning material did not exhibit any signs of degradation while under load at 533°K (500° F).

TABLE 2. SEALANT FORMULATIONS BASED ON VITON C-10 AND VITON LM

Ingredient	Dupont Formulation (Parts by Weight)	Modified Formulation (Parts by Weight)
Viton C-10	50	50
Viton LM	50	50
Magnesia (low activity)	5	5
MT Carbon Black	15	15
FS-1265 Fluorosilicone Oil (0.001 m ² /sec; 1000 cs)	10	2.5
Methyl Ethyl Ketone (MEK)	40	
Methyl Isobutyl Ketone (MIBK)		40
Ketimine (Epon Curing Agent H-2)	2	2

TABLE 3. SUMMARY OF AVERAGE LAPSHEAR TENSION DATA AT 533° K (500° F) FUEL VAPOR FOR 70-HOUR PERIODS

Sealant Type Designation Primer No.	Viton C-10/LM	Viton C-10	Fluorosilicone							
			94-002	94-030	94-516			77-028 ^a		
			DC-1200	92-047	None	92-040	92-051	77-006	77-006	77-006
	N/m ² × 10 ⁶ (psi)									
Control Specimens	4.41 (640)	9.79 (1420)	1.88 (273)	3.07 (445)	1.03 (149)	3.17 (460)	1.88 (273)	4.67 (678)	4.31 (625)	4.11 (596)
JP-4 Fuel Exposed	2.82 (409)	3.34 (484)	0.10 (15)	0.36 (52)	0.53 (77)	0.53 (77)	0.53 (77)	2.70 (391)	3.47 (504)	2.99 (434)
MIL-J-5161 Grade II Fuel Exposed	1.90 (275)	2.70 (392)	0	0.10 (15)				1.63 (236)	1.68 (244)	2.70 (393)

a. 77-028 is an improved version of 94-516.

As can be noted, of the three specimens exposed to the Viton C-10 sealant, two failed under load after 353 and 292 hours, respectively. The other did not fail after 1000 hours, but it did exhibit extensive stress corrosion cracking. It was deduced that electrochemical dissolution of the metal was the mechanism of failure.

Thus, it would appear from these studies that the fully-fluorinated and fluorosilicone classes of sealants would have the best compatibility with titanium alloys at the elevated temperatures associated

with advanced high speed aircraft. It would also appear from the sealant characterization phase of the program that the Dow Corning 77-028 sealant and the Viton C-10 sealant offer the most promise from that standpoint.

TASK C

This program is entitled "Prediction of Service Life of Polymeric Sealant Compositions for Fuel Tanks in Advanced Aerospace Structures from Measurement of Viscoelastic Properties." The

TABLE 4. SUMMARY OF LONG TERM COMPATIBILITY AT 533°K (500° F) BETWEEN TI-6Al-4V AND FLUORINATED SEALANTS

Applied Stress = $568.82 \times 10^6 \text{ N/m}^2$ (82.5 ksi)				
Sealant	Failure Time t_F , hours	Post Exposure Properties		
		Test Temperature, °K (°F)	Tensile Strength, $\text{N/m}^2 \times 10^6$ (ksi)	Yield Strength, $\text{N/m}^2 \times 10^6$ (ksi)
Viton C-10 (with Viton LM)	1000 ^a	RT ^b	875.63 (127)	—
	353	—	—	—
	292	—	—	—
Viton C-10 (without Viton LM)	625 ^a	RT	1254.85 (182)	1096.27 (159)
	625 ^a	RT	1234.16 (179)	1068.69 (155)
DC 94-516	1000 ^a	RT	1179.0 (171)	1089.37 (158)
Teflon	1000 ^a	RT	1199.69 (174)	1096.27 (159)
Kel-F 3700	1000 ^a	RT	414.37 (60.1)	386.11 (56)

a. No failure occurred within time indicated.

b. RT = Room temperature.

ultimate practical objective of this program was the development of a reasonably short duration test program based on measurements of the viscoelastic properties of polymeric sealant materials.

The principal initial effort in this program was aimed at development of reliable measurements of the effects of aging on physical and rheological properties. The parameters that were studied included (1) weight and volume, (2) Shore A hardness, (3) tensile and stress relaxation, (4) torsional damping, and (5) single lapshear strength. It was envisioned that these measurements could be extended or extrapolated to provide reliable estimates of the behavior of candidate sealants under cyclic fuel tank conditions for a period of 50 000 hours.

Three representative sealants were studied in this program: a Viton sealant supplied by the Air Force Materials Laboratory, and Dow Corning's

94-030 and 94-516 fluorosilicone sealants. The Air Force material consisted of 45 parts Viton B and 55 parts extracted Viton LM.

In actual experimental work, microtensile specimens of the three sealants were exposed to air and fuel (both liquid and vapor) at 373.15, 423.15, and 523.15°K (100, 150, and 250°C), and the values of the various parameters were determined at these temperatures. The collected data showed that the weight, volume, and Shore hardness of the three sealants were significantly changed through their exposures to air and fuel. The extremely vast amount of data that was collected during the duration of the program precludes its being presented at this time. The values of the other parameters were also affected through the environmental exposures.

In short, it must be stated that the primary objective, the development of a short-term test

method to predict the service life of sealants for fuel tanks for advanced aerospace vehicles, was not achieved in the first year's effort. However, insight was gained regarding typical commercially available sealants with respect to their performance under specified environmental conditions.

CONCLUSIONS

The current efforts of the in-house sealant program indicate that the silphenylene-siloxane polymer, suitably modified by the incorporation of fluorine-bearing aromatic substituents, is a strong candidate sealant material. The increased thermo-oxidative stability of the silphenylene-siloxane system, its ease of processing by standard sealant technology, and the anticipated degree of fuel resistance conferred by fluoro-aryl substituents all point to the possible utilization of this material as an improved alternate to the currently used commercial fluorosilicone.

The poly(perfluoroalkyletherisocyanurate) sealant materials under contracted development in Task A have been pursued successfully through prototype polymer preparation. These materials have demonstrated suitable thermal, oxidative, hydrolytic, and fuel stability, and the current efforts to prepare the higher molecular weight polymer precursor

should result in elastomeric properties. The modified polyimide sealants have not proven especially promising to date, but further structural modifications may result in more acceptable thermal and fuel stability.

Several conclusions were reached concerning the commercial fluorocarbon and fluorosilicone sealants tested in the Task B effort. Both materials apparently withstood the thermal/fuel exposure reasonably well. The Viton C-10 and Kel-F sealant materials can initiate stress corrosion cracking in Ti-6Al-4V alloy within 1000 hours at 533°K (500° F) under applied stress. Neither the perfluorinated or fluorosilicone sealant materials appeared to initiate stress corrosion cracking as indicated above. Finally, electrochemical dissolution of the titanium alloy metal has been assigned as the mechanism of failure.

Some definition of the Task C problem of service life prediction for viscoelastic materials has been achieved. However, the overall problem is more complex than anticipated and will require the acquisition of additional different type data before reliable service life predictions can be made. The rheological characteristics of the three sealants studied in this program vary widely and show that the mechanisms responsible for the changes in these characteristics are different from sealant to sealant.

ADHESIVES FOR HIGH PERFORMANCE VEHICLE APPLICATIONS

By

W. E. Hill

It should be noted initially that "high performance" refers to vehicle and not to adhesives. The term "high performance" is at best a subjective descriptor, but when applied in common usage to adhesives, it carries implications of ultrahigh strengths or ultrahigh temperature capability. This is not a high performance adhesive system that will be discussed here; it is a specialty adhesive with properties tailored to exacting safety standards adopted for materials in certain areas of manned spacecraft.

Reference is made to those areas of a spacecraft where structural materials may come into contact with liquid oxygen or those areas, such as the crew quarters, where the concentration of atmospheric oxygen is particularly high. A dependable structural adhesive with the following special qualifications is needed:

1. **Compatibility with liquid oxygen:** A liquid oxygen compatible material is defined as one that does not ignite, burn, char, or explode when tested in accordance with MSFC-SPEC-106B, which prescribes the conditions and criteria for standard impact testing in the presence of liquid oxygen.

2. **Nonflammability in enriched oxygen atmospheres:** The requirement for nonflammability means that the adhesive shall not ignite, burn, char, or explode when tested in accordance with MSFC-SPEC-101.

3. **Structural strengths at cryogenic temperatures:** Bond strength is, of course, the functional purpose of an adhesive. Structural bond strengths are arbitrarily defined as 70 kg/cm² (1000 psi) or above, and these strength levels at temperatures of liquid hydrogen require an adhesive that has a moderate degree of inherent flexibility.

In adhesive applications where the previously stated criteria of oxidative stability are not imposed, the polyurethane polymers have proven more than satisfactory at cryogenic temperatures. These

conventional polyurethanes, however, are not lox compatible. Some highly fluorinated polymers, such as Teflon FEP or TFE, are compatible with liquid oxygen and, under the proper conditions, will form bonds that have cryogenic capability. However, the circumstances for bond formation using Teflon as an adhesive are very drastic and unattainable for most applications. It appeared, therefore, that a processable polymer combining a high degree of fluorination with the cryogenically servicable polyurethane linkage would meet the service requirements for the program. Specifically, a highly fluorinated polyurethane would be expected to possess both a high degree of oxidative stability and acceptable low temperature mechanical properties. This combination has been effected through a research program undertaken by the Research and Development Division of Whittaker Corporation under contract to Marshall Space Flight Center. The result is a highly fluorinated polyurethane that exhibits the desired engineering properties at cryogenic temperatures, together with a low sensitivity toward liquid oxygen and nonflammability in gaseous oxygen.

Emergence of a new technology of fluorinated polyurethanes was made possible by two developments:

1. Synthesis of a number of previously unknown fluorinated aromatic diamines and diisocyanates. The diisocyanates are, of course, prepared directly from the fluorinated diamines. Preliminary screening indicated the urethane linkage resulting from reaction between isocyanate and hydroxyl groups is inherently lox compatible. Evaluation of several different diisocyanates showed 1-chloro-2,4-diisocyanato-3,5,6-trifluorobenzene to be the kinetic choice for this program.

2. Utilization of the hydroxyl terminated polyether of perfluoropropylene oxide as the glycol component of the polyurethane resin (Fig. 1). The ether linkages provide flexibility, and preliminary screening indicated no problem with lox compatibility of ethers of this type.

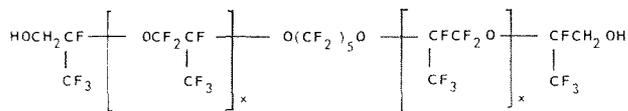


Figure 1. Hydroxyl terminated polyether of perfluoropropylene oxide.

Reaction between the diisocyanate monomer and the glycol prepolymer gives the linear fluorinated polyurethane. Cross-linking, or curing, is accomplished through allophanate formation when excess diisocyanate reacts with the NH sites indicated by the arrows (Fig. 2). In practice, a 1.8 ratio of isocyanate to hydroxyl is employed when the adhesive components are mixed for application to the adherend surface, along with a small amount of soluble metal catalyst favoring the formation of urethane and allophanate linkages. Typical of the first successful formulations was a polymer of this type made with 0.1 percent ferric naphthenate as catalyst, and having these properties:

1. The polymer was tox compatible.
2. The polymer was not ignited in standard flammability testing, although it did melt.
3. Tensile bond strengths on aluminum adherends were 350 kg/cm² (5000 psi) at 77.15°K (-320° F), 105 kg/cm² (1500 psi) at 297.15°K (75° F), and 10.5 kg/cm² (150 psi) at 366.15°K (200° F).

The outstanding deficiencies were poor tear strength and very poor elevated temperature strength. Another

objection to this formulation is that the diisocyanate monomer, before mixing, is highly toxic so that the bonding operation must be conducted with deliberate care.

A current objective of this program is to modify the cross-linking mechanisms in a manner to improve thermal stability and strength at elevated temperatures. Additional applications have been proposed for this polymer system, since its property of non-flammability recommends it for conformal coating and electronic embedment utilization. These electronic packaging applications require retention of a certain amount of pre-cure fluidity, and any modification designed to improve the cross-linking of the cured polymer must be commensurate with this requirement.

Three modifications have been made in the basic system just described. The first modification does not change the basic structure, but simply incorporates the toxic diisocyanate monomer into the system as a prepolymer, where it is no longer toxic, thus eliminating a health hazard in using this system. This is accomplished by treating the fluorinated glycol with the fluorinated diisocyanate in the absence of catalyst, producing the isocyanate capped prepolymer. The cure reaction is then initiated at the time of the bonding operation by incorporation of additional fluorinated glycol and a catalyst to accelerate the allophanate cross-linking reaction (Fig. 3).

The second modification again proceeds through the isocyanate capped prepolymer and employs cyanuric trihydrazide as a trifunctional curing agent. The isocyanate capped prepolymer, shown previously, is reacted with cyanuric trihydrazide to yield a highly cross-linked polymer (Fig. 4). The product

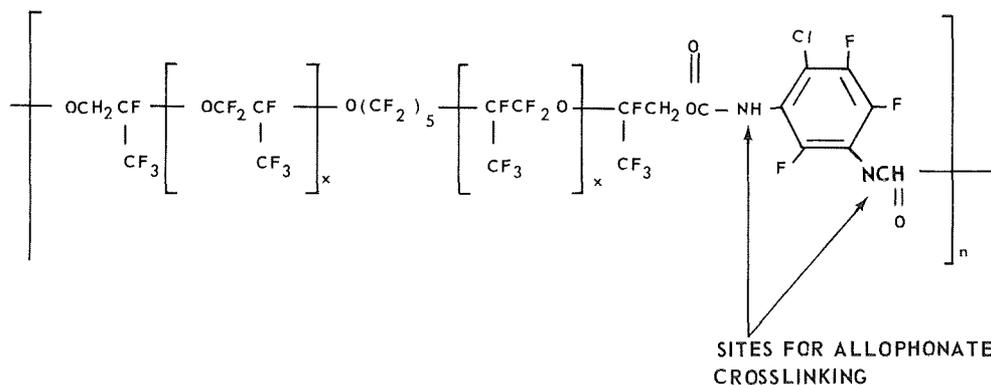


Figure 2. Linear fluorinated polyurethane.

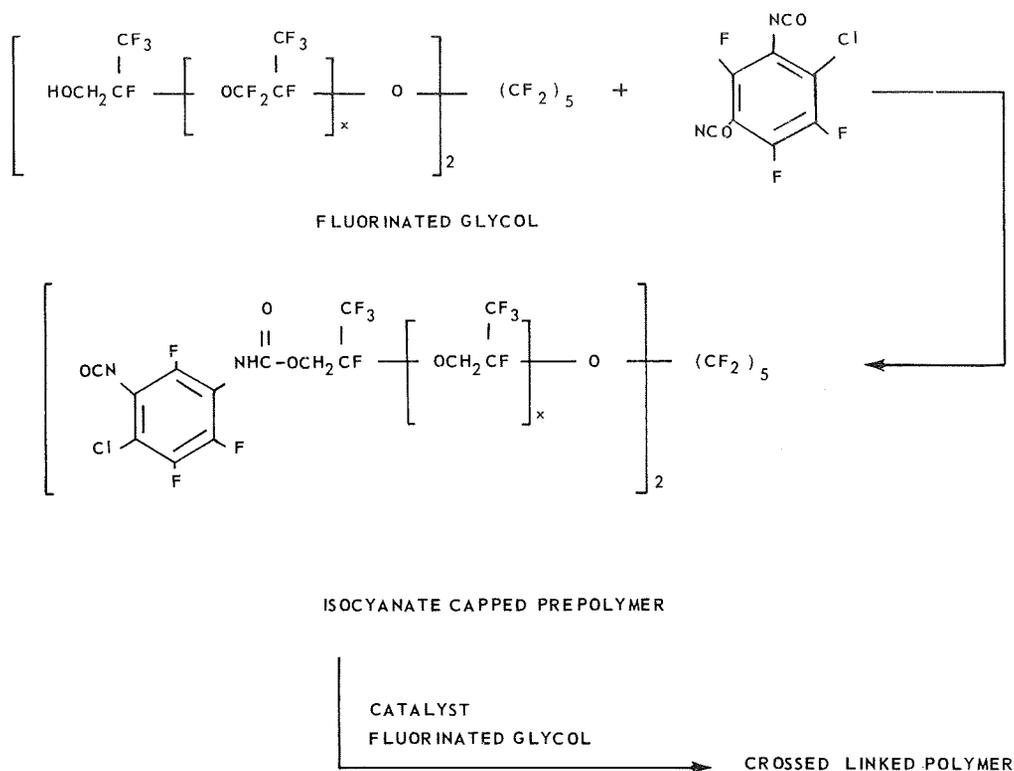


Figure 3. Preparation and cross-linking of isocyanate capped prepolymer.

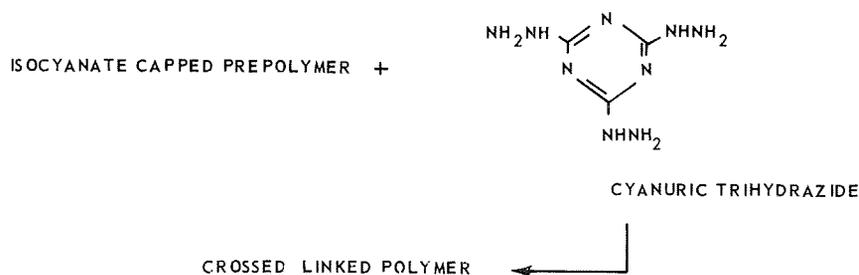


Figure 4. Cyanuric trihydrazide as a cross-linking agent.

was nonflammable, fairly strong, and quite stiff. Cure was too rapid (5 minutes) to permit bonding processing, however.

The third modification was designed to continue use of a trifunctional curing agent and yet decrease somewhat the cross-link density, thus achieving a more elastomeric product. A portion of the isocyanate capped prepolymer is recapped with melamine, and the melamine capped prepolymer is used along with the fluorinated diol plus a quantity of the diisocyanate to yield a cross-linked polymer (Fig. 5). Variations of the relative proportions of the two prepolymers, the fluorinated glycol, and the diisocyanate

permit a broad range of possible formulations. This is a very recent development, and no polymer properties are reportable.

In summary, then, there is a requirement for an adhesive system compatible with liquid oxygen and nonflammable in an enriched oxygen atmosphere. These requirements are met by a highly fluorinated polyurethane system, which, however, has poor strength properties in the higher temperature regions of its use range. Improved cross-linking is the answer to improved thermal stability and is the purpose of polymer modification now under study.

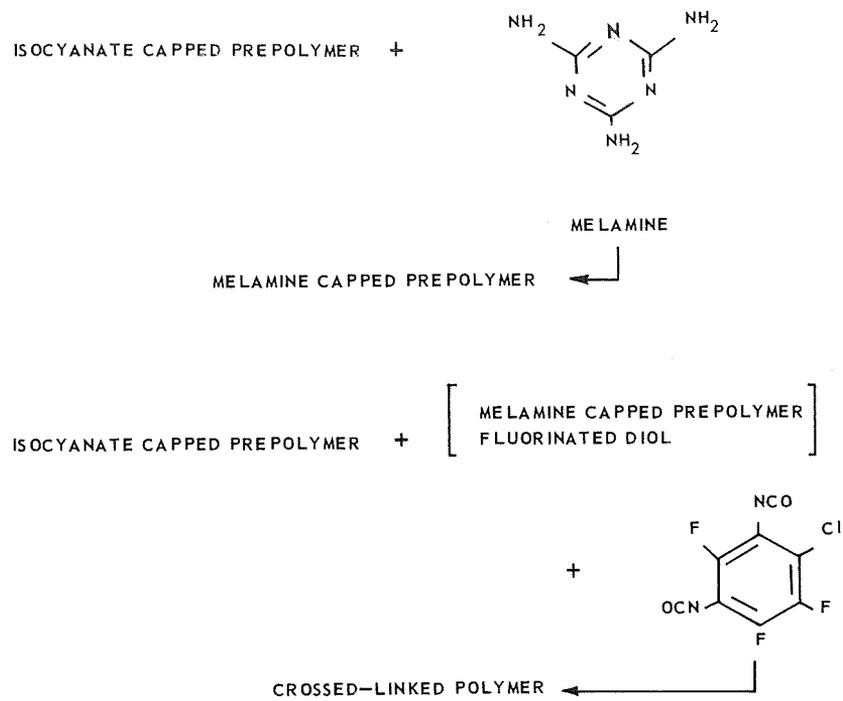


Figure 5. Melamine as a cross-linking agent.

FLAMMABILITY CONSIDERATIONS FOR SPACE STATION/SPACE SHUTTLE

By

C. F. Key

SUMMARY

Flammability studies at MSFC have revealed a number of interesting phenomena that affect the selection of materials for closed ecological systems such as spacecraft and space stations. The major items discussed in this paper are the effect of sample thickness, effect of oxygen concentration, effect of chemical composition, and ignitor effects.

COMPARATIVE CONSIDERATIONS OF FIRE RISKS IN SPACE VERSUS EARTH

The fire hazards associated with the use of spacecraft atmospheres consisting of pure or enriched oxygen are well known. However, the risks resulting from a fire in a spacecraft compared to earth fires is

not generally made evident. A comparison of these risks is made in Table 1.

It is readily concluded from Table 1 that spacecraft fires are much more hazardous because of the higher oxygen concentration and the lesser possibility of escape. For example, if a fire occurs in a building, there are numerous ways a person could escape the building or at least retreat to a place to await rescue; however, in the event of a spacecraft fire, the astronauts cannot retreat to a safe area, because presently designed spacecraft do not have compartments such as normal ships. Also, the danger of the spacecraft rupturing because of the fire would present additional hazards most likely resulting in loss of the crew. In addition, the effect of damaging various systems, such as the electrical or oxygen replenishing systems, would probably be a loss of lives. Therefore, it is evident that spacecraft materials selection must be more stringent than normally required on earth to preclude these catastrophic events.

TABLE 1. COMPARATIVE CONSIDERATIONS OF FIRE RISKS IN SPACE VERSUS EARTH

Factor	Earth	Space
Composition	21 percent O ₂ 103 421. 4 N/m ² (15 psia)	21 to 100 percent O ₂ 34 473. 8 to 103 421. 4 N/m ² (5 to 15 psia)
Propagation Rate	—	High in Most Designs
Toxic Effects	Negligible	Serious
Smoke Effects	Appreciable	Very Serious
Temperature	Negligible	Catastrophic
Burst Pressure	Negligible	Catastrophic
Escape	Normally Excellent	Very Limited
System Consequences	Normally Survivable	Normally Critical to Life

FIRE TRIANGLE

The three elements comprising the fire triangle are shown in Figure 1. All three elements shown must be present for a fire to occur. It is virtually impossible to eliminate the oxygen leg in spacecraft because of the necessity for the habitation environment. Therefore, the most practical ways to prevent fires is to eliminate the ignition source and to restrict the use of certain materials.

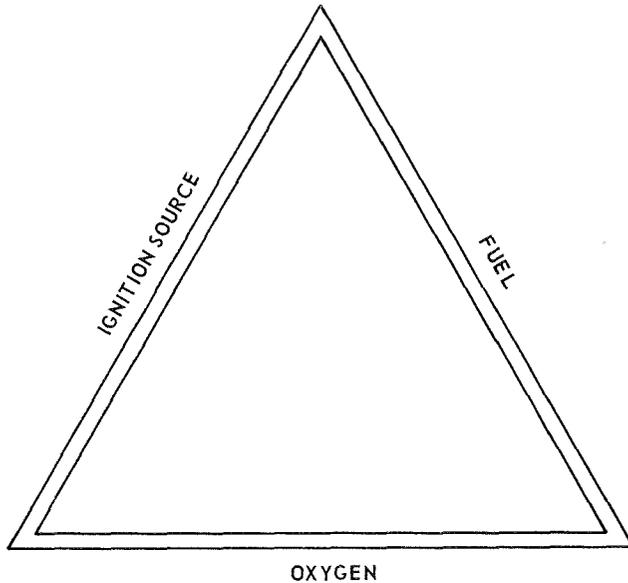


Figure 1. Fire triangle.

IGNITION SOURCES

The sources of ignition in a manned space station are caused by internal or external stimuli as shown in Table 2. The internal ignition sources result from electrical components, shorting, overheating, and arcing. Additional internal ignition sources are attributable to the various experiments (i. e. ; flammability, welding, etc.) and the additional motors, fans, and materials brought aboard to conduct the various experiments.

The external ignition sources result entirely from micrometeoroid penetration. Micrometeoroid penetration can initiate burning by direct ignition, shock wave, and spalling debris from the impact. Bumpers applied exterior to the spacecraft reduce

the probability of micrometeoroid penetrations to an acceptable level.

TABLE 2. IGNITION SOURCES

In Spacecraft:	
Electrical	— Shorts, Overheating, Arcing, etc.
Experiments	— Flammability, Motors, Fans, Materials
External:	
Micrometeoroid Penetration	— Direct Ignition, Shock Wave, Spalling Debris

APPROACH TO FIRE PREVENTION

The approaches to fire prevention are shown in Table 3. The primary approach to fire prevention is to insure that the materials, in thicknesses intended for use, are nonflammable in their application in the anticipated environment. Additional approaches include methods for minimizing electrical shorts and other ignition sources and encouraging reduction in oxygen concentrations for manned spacecraft.

TABLE 3. APPROACH TO FIRE PREVENTION

Primary	— Control of Fuels Nonflammable in Anticipated Environment
Additional	— Minimize Electrical Shorts and Ignition Sources — Encourage Reduction in Percent of O ₂
Thus	— Flammability of Materials is Primary Concern in Fire Prevention in Habitable Areas

DESIGN REQUIREMENTS FOR HABITATION

The design requirements for materials in their use application to insure that the crew will survive any fire are listed in Table 4.

TABLE 4. DESIGN REQUIREMENTS
FOR HABITATION

Nonflammable per Appropriate Screening Test
Nonflammable under Simulated Operating Conditions
Non-noxious and Nontoxic during Outgassing Conditions
Design Burst Pressure of Structure Must not be Exceeded if Burning is Experienced
Bulk Gas Temperature Must be Maintained at Tolerable Level for Crew if Burning is Experienced
Mechanical and Physical Integral during Launch and Orbital Environments

IGNITOR EFFECTS

There are currently two ignitor systems used by NASA to evaluate the flammability of materials in enriched oxygen environments. NASA Manned Spacecraft Center's flammability document MSC D-NA-002,

"Procedures and Requirements for the Flammability of Offgassing Evaluation of Manned Spacecraft Non-metallic Materials," specifies the use of a silicone ignitor, whereas MSFC-SPEC-101, "Flammability Requirements and Test Procedures for Materials in Gaseous Oxygen Environments," specifies the use of a nichrome wire ignitor. The paper stick ignitor is considered to be a compromise between the silicone and hot wire.

A test program was initiated at MSFC to evaluate the severity of these ignition schemes. The results of this program are listed in Table 5. It is evident that the silicone ignitor is more severe than either the paper stick or nichrome ignitors. As expected, the paper stick ignitor is more severe than the nichrome ignitor and less severe than the silicone ignitor. It is also evident from this study that the use of larger samples is mandatory if the silicone ignitor is used.

FLAME PROPAGATION RATE
IN VARIOUS ATMOSPHERES

A comparison of the increased flammability hazard as oxygen concentration is increased is

TABLE 5. IGNITOR EFFECTS^a

	Nichrome	Silicone	Paper Stick
Refset L3236 [0.178 cm (0.070 in.) thick]	NI ^b	SE [7.62 cm (3.0 in.)]	SE [0.635 cm (0.25 in.)]
L3203-6 [0.318 cm (0.125 in.) thick]	NI	SE [1.27 cm (0.5 in.)]	NI
Fluorogreen E-600 [0.178 cm (0.070 in.) thick]	NI	SE [2.54 cm (1.0 in.)]	SE [1.27 cm (0.5 in.)]
Refset 3489 [0.020 cm (0.008 in.) thick]	NI	SE [7.62 cm (3.0 in.)]	SE [2.54 cm (1.0 in.)]
L-3217-1 [0.183 cm (0.072 in.) thick]	NI	BC ^d	BC
Teflon FEP [0.635 cm (0.250 in.) thick]	SE ^c [1.27 cm (0.5 in.)]	SE [0.635 cm (0.25 in.)]	SE [0.635 cm (0.25 in.)]
M385-10 [0.025 cm (0.010 in.) thick]	NI	BC	SE [10.16 cm (4.0 in.)]

a. Bottom Ignition — 100 percent O₂ — 41 368.5 N/m²

b. NI = No Ignition

c. SE = Self-Extinguishing

d. BC = Burns Completely

tabulated in Tables 6 and 7. It is readily seen that flame propagation rates increase drastically from air to 100 percent oxygen at various pressures.

EFFECT OF THICKNESS

The data tabulated in Table 8 indicate that there are basically two types of materials. One type (cellulose, butyrate, polycarbonates, etc.) is flammable [100 percent oxygen at 41 368.5 N/m² (6 psia)] in all thicknesses; whereas, for the other type (highly fluorinated and polyimide laminate), a thickness has been detected at which, for all practical purposes, it is nonflammable.

SAMPLE ORIENTATION

Tabulated in Table 9 are the results of sample orientation on flame propagation rates. It is readily seen that the burning characteristics of materials are affected by the sample orientation.

EFFECT OF CHEMICAL COMPOSITION

The flammability hazard of organic materials is related to chemical composition in addition to thickness. Comparisons of this effect are shown in Tables 10 and 11. Polyethylene is highly flammable,

but as fluorine is introduced into the parent compound, the flammability is reduced (top ignition).

It is well known that processing additives and fillers affect lox compatibility of materials; therefore, it is not surprising that these additives and fillers affect flammability of materials. The variation of flame propagation rates of various polyurethane foams with different cure agents and additives is shown in Table 11.

SPACE SHUTTLE FLAMMABILITY

The gas composition of the Space Shuttle and Space Station will be air at 101 352.9 N/m² (14.7 psia) or slightly enriched air [30.9 percent oxygen at 68 947.6 N/m² (10 psia)] as shown in Table 12. The Federal Aeronautics Administration (FAA) requirement for aircraft is also shown in Table 12. The FAA criteria are generally more severe than MSFC-SPEC-101 and MSC D-NA-0002, if the test environment is the habitation environment. However, the increased sample and burning length may permit the use of a wider range of materials than either of the NASA specifications. A working group, chaired by NASA Headquarters, is working toward a consolidated specification, and tentative agreement indicates a larger sample and criteria similar to FAA.

TABLE 6. FLAME PROPAGATION RATES IN VARIOUS ATMOSPHERES^a

	Air	46 percent O ₂ / 54 percent N ₂	70 percent O ₂ / 30 percent N ₂	100 percent O ₂
Pressure	101 352.9 N/m ² (14.7 psia)	51 710.7 N/m ² (7.5 psia)	34 473.8 N/m ² (5 psia)	34 473.8 N/m ² (5 psia)
Paper	0.203 cm/sec (0.08 in./sec)	1.02 cm/sec (0.4 in./sec)	1.52 cm/sec (0.6 in./sec)	2.29 cm/sec (0.9 in./sec)
Cellulose Acetate	0.0203 cm/sec (0.008 in./sec)	0.254 cm/sec (0.1 in./sec)	0.508 cm/sec (0.2 in./sec)	0.762 cm/sec (0.3 in./sec)
Cotton	0.254 cm/sec (0.1 in./sec)	2.29 cm/sec (0.9 in./sec)	5.08 cm/sec (2.0 in./sec)	8.13 cm/sec (3.2 in./sec)
Nylon	NB ^b	1.219 cm/sec (0.48 in./sec)	1.346 cm/sec (0.53 in./sec)	2.108 cm/sec (0.83 in./sec)

a. Top Ignition

b. NB = Nonburning

TABLE 7. PROPAGATION RATE VERSUS PRESSURE^a

	Air	34 473.8 N/m ² (5 psia)	68 947.6 N/m ² (10 psia)	89 631.8 N/m ² (13 psia)
Adiprene L-167	SE ^b	48.26 cm/min (19 in./min)	66.04 cm/min (26 in./min)	78.74 cm/min (31 in./min)
Butyl Rubber	SE	8.13 cm/min (3.2 in./min)	15.24 cm/min (6 in./min)	20.83 cm/min (8.2 in./min)
Hypalon	SE	5.59 cm/min (2.2 in./min)	7.87 cm/min (3.1 in./min)	9.14 cm/min (3.6 in./min)
Narmco 7343	SE	31.50 cm/min (12.4 in./min)	54.10 cm/min (21.3 in./min)	66.04 cm/min (26 in./min)
Natural Rubber	SE	10.41 cm/min (4.1 in./min)	13.46 cm/min (5.3 in./min)	15.75 cm/min (6.2 in./min)
Polyacrylate	SE	8.38 cm/min (3.3 in./min)	16 cm/min (6.3 in./min)	18.29 cm/min (7.2 in./min)
Polyurethane Foam	SE	1280.16 cm/min (504 in./min)	1686.56 cm/min (664 in./min)	2819.4 cm/min (1110 in./min)
PR-1527	SE	45.72 cm/min (18 in./min)	50.8 cm/min (20 in./min)	81.28 cm/min (32 in./min)

a. Top Ignition — 100 percent O₂

b. SE = Self-Extinguishing

TABLE 8. THICKNESS EFFECTS^a

Two Classes of Materials:	
1. Flammable ^a in all Thicknesses but Flame Propagation Rates Inversely Proportional to Thickness	
Cellulose Butyrate, Lexan, etc.	
12.7 × 10 ⁻⁵ m (5 mils)	241.3 cm/min (95 in./min)
2.54 × 10 ⁻⁴ m (10 mils)	152.4 cm/min (60 in./min)
12.7 × 10 ⁻⁴ m (50 mils)	88.9 cm/min (35 in./min)
20.32 × 10 ⁻⁴ m (80 mils)	60.96 cm/min (24 in./min)
6.35 × 10 ⁻³ m (250 mils)	25.4 cm/min (10 in./min)
2. Nonflammable in Certain Thicknesses	
Teflon TFE	7.92 × 10 ⁻⁶ m (0.312 mils)
Teflon FEP	6.35 × 10 ⁻⁶ m (0.250 mils)
Refset L-3236	2.29 × 10 ⁻⁶ m (0.090 mils)
Teflon Coated Fiberglass	0.25 × 10 ⁻⁶ m (0.010 mils)
L3203-6	1.52 × 10 ⁻⁶ m (0.60 mils)
KEL-F	6.35 × 10 ⁻⁶ m (0.250 mils)
Polyimide Laminates	1.02 × 10 ⁻⁶ m (0.040 mils)

a. Top Ignition — 41 368.5 N/m² (6 psia)

TABLE 9. SAMPLE ORIENTATION [Flame Propagation Rate — 100 percent O₂ at 42 747.5 N/m² (6.2 psia)]

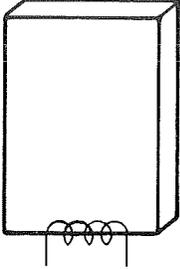
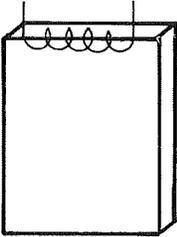
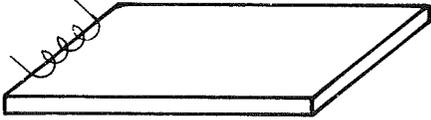
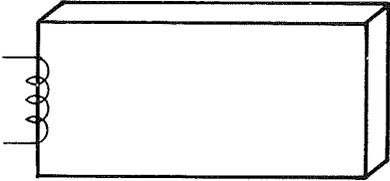
	Cyclac H-4001	Silicone	Acrylic
	121.92 cm/min (48 in./min)	20.83 cm/min (8.2 in./min)	49.53 cm/min (19.5 in./min)
	23.37 cm/min (9.2 in./min)	8.64 cm/min (3.4 in./min)	16.51 cm/min (6.5 in./min)
	37.85 cm/min (14.9 in./min)	7.87 cm/min (3.1 in./min)	27.18 cm/min (10.7 in./min)
	16.51 cm/min (6.5 in./min)	5.33 cm/min (2.1 in./min)	15.49 cm/min (6.1 in./min)

TABLE 10. CHEMICAL COMPOSITION^a

Polyethylene	- (CH ₂ - CH ₂) _N -	45.72 cm/min (18 in./min) ^a
Polyvinyl Fluoride	- (CH ₂ - CFH) _N -	40.64 cm/min (16 in./min)
Polyvinylidene Fluoride	- (CF ₂ - CH ₂) _N -	7.62 cm/min (3.0 in./min)
Chlorotrifluoroethylene	- (CF ₂ - CFCl) _N -	Self Extinguishing
Tetrafluoroethylene	- (CF ₂ - CF ₂) _N -	No Ignition
Fluoroethylene Propylene	- (CF ₂ - CF ₂ - CF ₂ - CF) _N - CF ₂	No Ignition

a. Top Ignition [1.27 × 10⁻⁴ m (5 mils) thick] — 100 percent O₂ — 41 368.5 N/m² (6 psia)

TABLE 11. POLYURETHANES — FLAME PROPAGATION RATES IN 100 PERCENT OXYGEN

3D Foam	914.4 cm/min (360 in./min) ^a
Isofoam	889 cm/min (350 in./min)
Foam Rubber	381 cm/min (150 in./min)
Uralane 577-1	91.44 cm/min (36 in./min)
Narmco 7343	31.5 cm/min (12.4 in./min)
Dynatherm D-65	38.96 cm/min (11.4 in./min)

a. Top Ignition — 41 368.5 N/m² (6 psia)

TABLE 12. SPACE SHUTTLE/STATION FLAMMABILITY

Gas Composition:	27 percent O ₂ in N ₂ at 82 737.1 N/m ² (12 psia) or 21 percent O ₂ in N ₂ at 103 421.4 N/m ² (15 psia)
<u>Federal Aeronautics Administration (FAA) Requirements</u>	
General Interior Materials — Self-Extinguishing in 15.24 to 20.32 cm (6 to 8 in.)	
Windows + Seat Belts — Maximum 6.35 cm/min (2.5 in./min) — Horizontal	
Baggage and Cargo Area — Self-Extinguishing in 15 seconds, 45 degrees	
Electrical System — Self-Extinguishing in 30 seconds — Horizontal	
<u>MSFC-SPEC-101 (AAP) Requirements [34 473.8 N/m² (5 psia) O₂]</u>	
General Materials — Noncombustible or Self-Extinguishing in 2.54 cm (1.0 in.) Vertical	
Wiring and Potting Compounds — Noncombustible or Self-Extinguishing in 2.54 cm (1.0 in.)	

TABLE 13. FUTURE PLANS

FUTURE RESEARCH AND DEVELOPMENT FLAMMABILITY STUDIES

MSFC has a continuing program to develop information regarding the flammability of materials. Some specific areas for which research and development flammability studies are currently being planned at MSFC are listed in Table 13.

<u>FAA Type</u>	Flammability Tests/Correlation with Prior Results
<u>Flammability Factors</u>	
	Effect 27 percent O ₂ at 82 737 N/m ² (12 psia) versus Air
	Configuration Testing
	Toxicity of Combustion Products
	Sample Size versus Ignitors
	Heat Sink Effects

APPROVAL

TM X-64521

RESEARCH ACHIEVEMENTS REVIEW
VOLUME III REPORT NO. 10

The information in these reports has been reviewed for security classification. Review of any information concerning Department of Defense or Atomic Energy Commission programs has been made by the MSFC Security Classification Officer. These reports, in their entirety, have been determined to be unclassified.

These reports have also been reviewed and approved for technical accuracy.


KARL L. HEIMBURG
Director, Astronautics Laboratory

UNITS OF MEASURE

In a prepared statement presented on August 5, 1965, to the U. S. House of Representatives Science and Astronautics Committee (chaired by George P. Miller of California), the position of the National Aeronautics and Space Administration on Units of Measure was stated by Dr. Alfred J. Eggers, Deputy Associate Administrator, Office of Advanced Research and Technology:

"In January of this year NASA directed that the international system of units should be considered the preferred system of units, and should be employed by the research centers as the primary system in all reports and publications of a technical nature, except where such use would reduce the usefulness of the report to the primary recipients. During the conversion period the use of customary units in parentheses following the SI units is permissible, but the parenthetical usage of conventional units will be discontinued as soon as it is judged that the normal users of the reports would not be particularly inconvenienced by the exclusive use of SI units."

The International System of Units (SI Units) has been adopted by the U. S. National Bureau of Standards (see NBS Technical News Bulletin, Vol. 48, No. 4, April 1964).

The International System of Units is defined in NASA SP-7012, "The International System of Units, Physical Constants, and Conversion Factors," which is available from the U. S. Government Printing Office, Washington, D. C. 20402.

SI Units are used preferentially in this series of research reports in accordance with NASA policy and following the practice of the National Bureau of Standards.

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* Classified. Proceedings not published.

** Proceedings summarized only.

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